

Table 2-3. Air Quality and Meteorological Routine Measurements at Existing Sites in the South Coast Region

Site Code	Sampling Site	03	NO/NOx	Gaseous		Pollutants Monitored					Meteorological Measurements				
				CO	S02	THC(a)	1NMHC (b)	TSP	Pb	S04	HiVol NO3	TOF (c)	PM10	Temp	Humidity
LOS ANGELES BASIN															
SURFACE															
1	Alhambra														X
2	Anaheim	X	X	X	X			X	X	X					X
3	Azusa	X	X	X	X	X		X	X	X	X	X			X
4	Banning	X						X	X						X
5	Burbank	X	X	X	X										X
6	Burbank AP											X	X		X
7	Cajon														X
8	Chino	X													X
9	Compton AP														X
10	Costa Mesa	X	X	X	X										X
11	El Toro	X	X					X	X	X	X				X
12	El Toro MB											X	X		X
13	Fontana	X	X	X	X			X	X	X	X				X
14	Glendora	X													X
15	Hawthorne AP														X
16	Hemet	X													X
17	John Wayne AP											X	X		X
18	La Habra	X	X	X	X	X		X	X	X	X				X
19	Lake Gregory	X	X	X	X	X		X	X	X	X				X
20	Lennox	X	X	X	X	X		X	X	X	X				X
21	Long Beach	X	X	X	X	X		X	X	X	X				X
22	Los Alamitos	X	X	X	X						X	X	X		X
23	Los Angeles	X	X	X	X	X	X				X	X	X		X
24	LAX											X			X
26	Lynwood	X	X	X	X										X
27	Malibu														X
28	March AFB										X	X	X		X
29	Mission Hills	X													X
30	Newhall	X													X
31	Norco	X													X
32	Norton AFB														X
33	Ontario AP											X	X		X
34	Pasadena	X	X	X	X			X	X	X	X				X
35	Perris	X	X	X	X			X	X	X	X				X
36	Pico Rivera	X	X	X	X			X	X	X	X				X
37	Pomona	X	X	X	X										X
38	Redlands	X	X									X			X
39	Redondo Beach														X
	Airport														
40	Reseda	X	X	X	X			X	X	X					X
41	Rialto														X
42	Riverside		X	X	X			X	X	X					X
43	Rubidoux	X	X	X	X	X		X	X	X	X				X

Table 2-3. (continued)

Site Code	Sampling Site	03	NO/NOx	Gaseous					Pollutants Monitored					Meteorological Measurements				
				C0	S02	THC(a)	NMHC (b)	TSP	Pb	S04	HiVol NO3	TOF(c)	PM10	Temp	Humidity	WS/WD (d)	Radiation	
44	San Bernardino	X	X	X	X			X	X	X	X		X			X		
45	San Juan Capistrano																	
46	Santa Monica AP													X	X	X		
47	Torrance AP	X	X	X	X									X	X	X		
48	Upland																	
49	Van Nuys													X		X		
50	Venice																	
51	Vernon																	
52	W. LA	X	X	X	X													
53	Whittier	X	X	X	X													
54	Zuma Beach																	
55	Beaumont													X	X	X		
56	Fullerton AP													X		X		
57	Mt. Wilson																	
58	Pomona AP																	
UPPER AIR																		
25	Loyola-																	
33	Marymount													X	X			
	Ontario AP	X												X				

Table 2-3. (continued)

Site Code	Sampling Site	03	NO/NOx	Gaseous CO S02	Pollutants Monitored				HiVol NO3	T0F(c) PM10	Temp	Meteorological Measurements		
					THC(a) NMHC (b)	TSP	Pb	S04				Humidity	WS/WD	Radiation
VENTURA COUNTY														
SURFACE														
59	Anacapa Is	X				X					X	X	X	X
	Casitas Pass												X	
	El Rio	X	X	X		X				X	X	X	X	X
	Laguna Peak									X	X	X	X	X
	Ojai	X				X				X	X	X	X	X
	Oxnard AP									X	X	X	X	X
	Piru	X				X				X	X	X	X	X
	Pt. Mugu									X	X	X	X	
	Rocketdyne	X								X	X	X	X	
	San Miguel Is									X	X	X	X	
60	Santa Barbara Is									X	X	X	X	
	Santa Cruz Is									X	X	X	X	
	Santa Rosa Is									X	X	X	X	
	Simi Valley	X	X	X	X	X	X	X	X	X	X	X	X	X
	Thousand Oaks	X												
	Upper Ojai													
	Ventura	X	X	X	X	X				X	X	X	X	
	UPPER AIR													
	61	Pt. Mugu									X	X	X	X
San Nicolas Is										X	X	X	X	

(a) THC = total hydrocarbon

(b) NMHC = non-methane hydrocarbon

(c) TOF = total benzene extractable organic fraction

(d) WS/WD = wind speed and wind direction

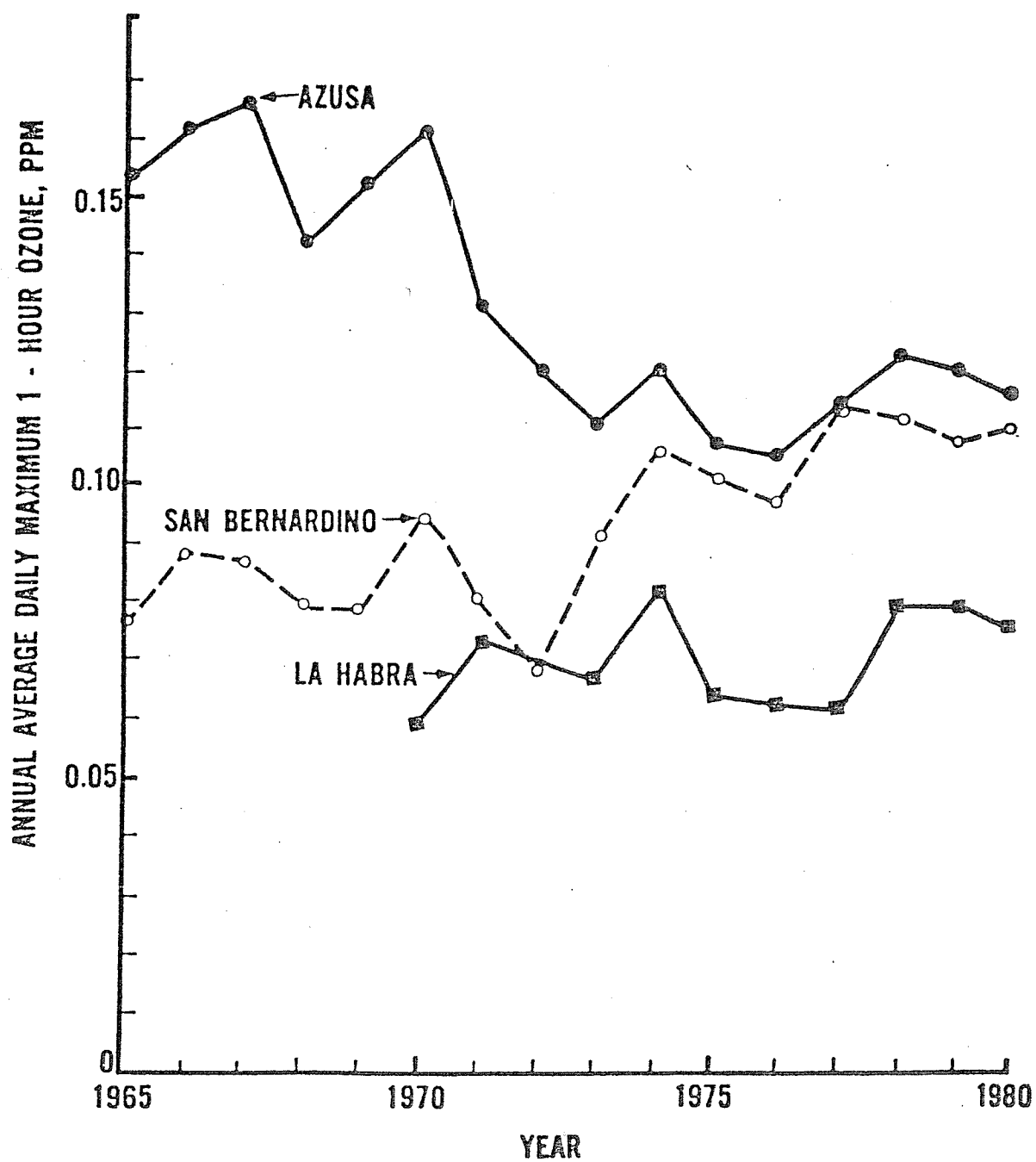


Figure 2-6a. Sixteen Year Trend in the Annual Average of Daily Maximum 1-Hour Ozone Concentration from 1965 to 1980 at Azusa, San Bernardino, and La Habra. (SCAQMD, 1981)

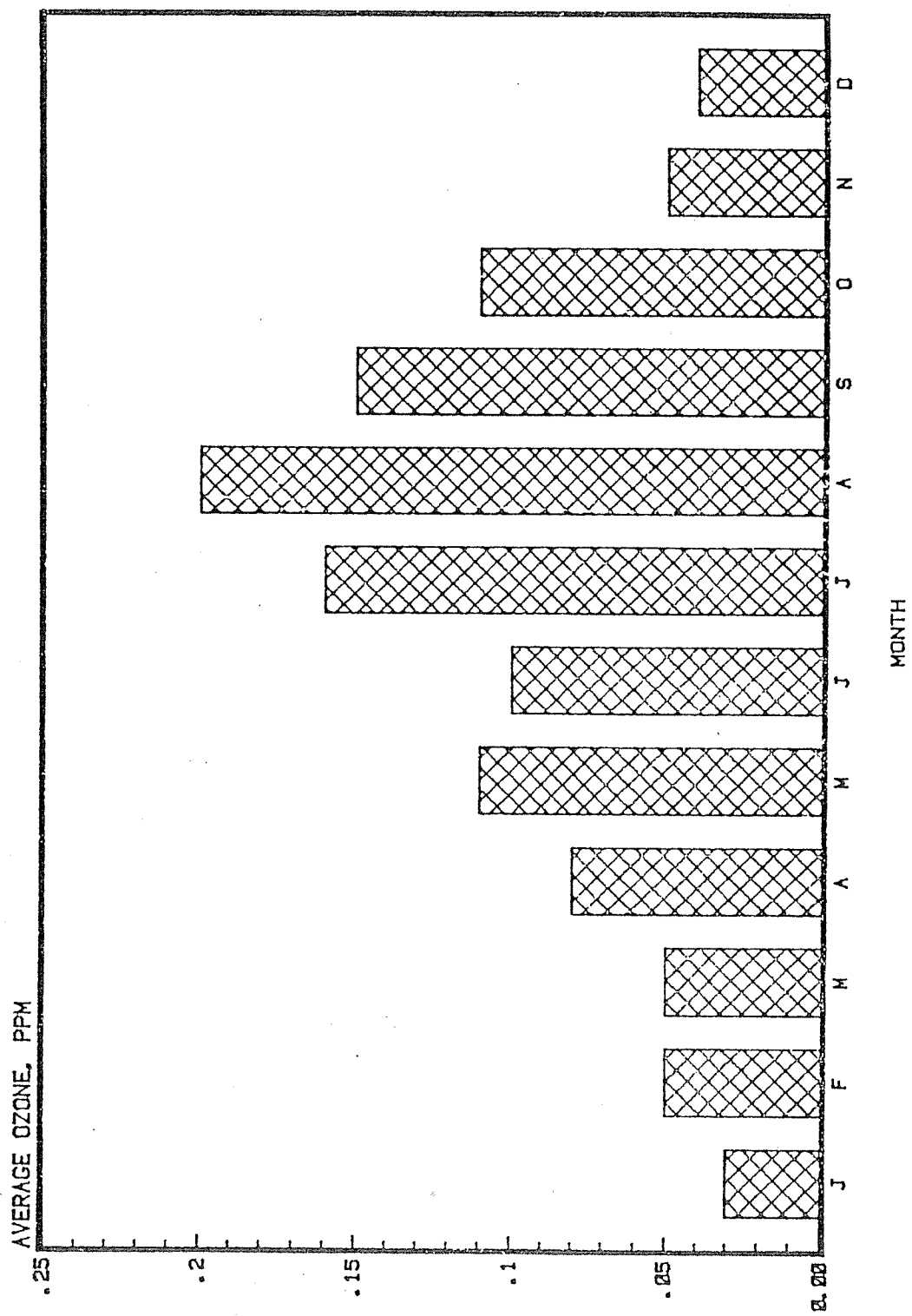


Figure 2-6b. 1982 Ozone Monthly Average of Daily 1-Hour Maximum at Azusa, CA. (Hoggan et al., 1983)

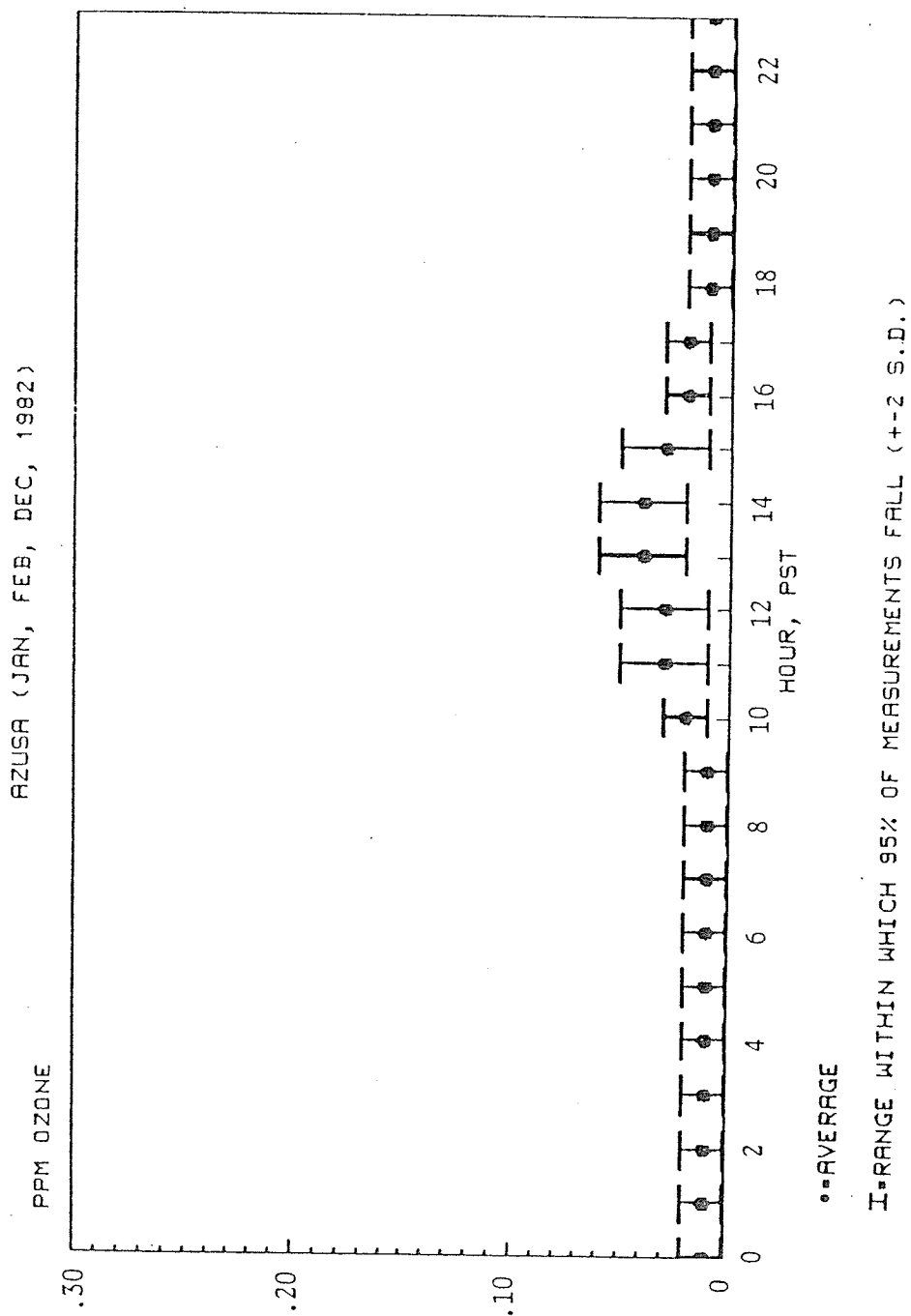


Figure 2-6c. 1982 Winter Average Ozone for Each Hour at Azusa, CA. (Hoggan et al., 1983)

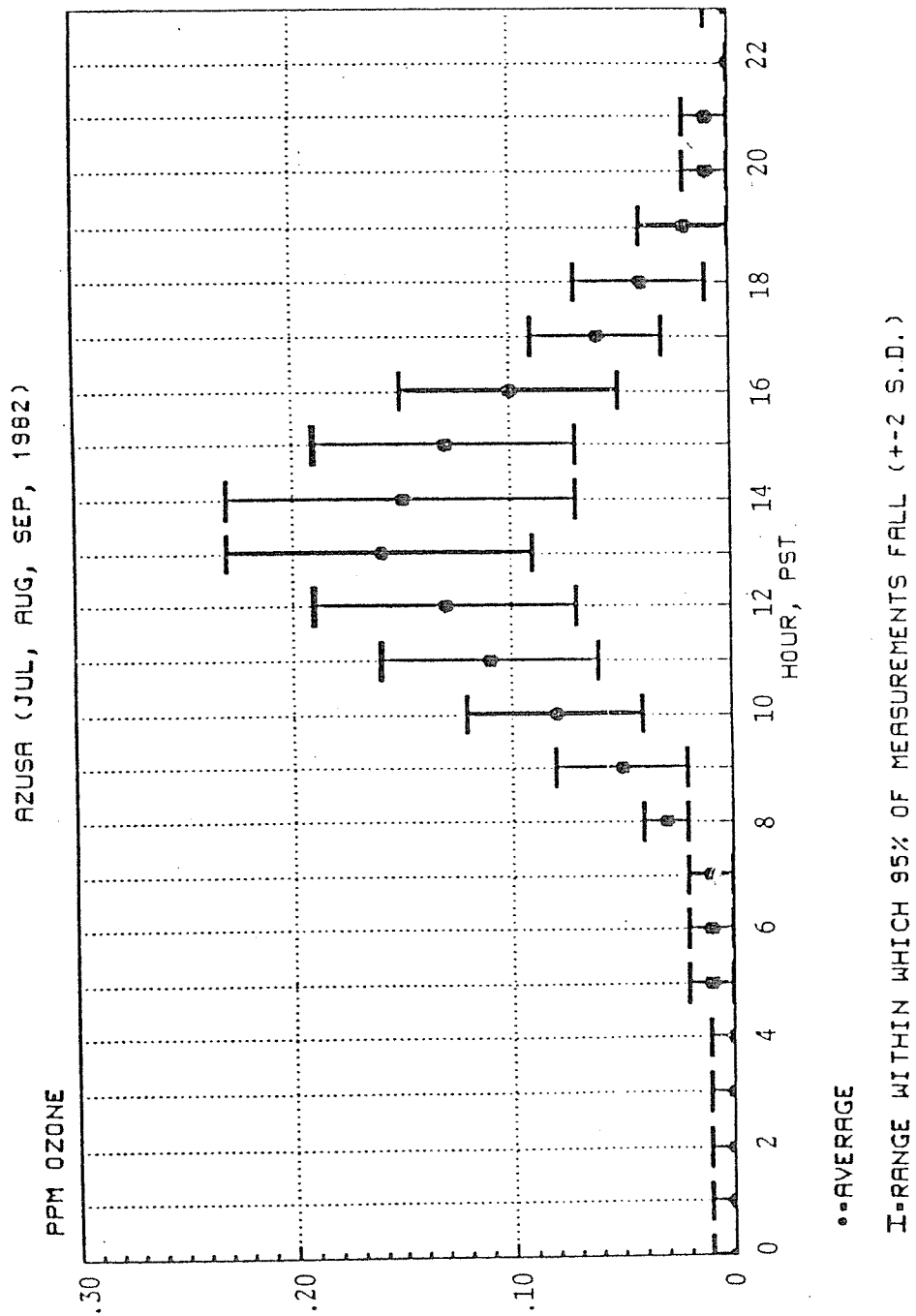


Figure 2-6d. 1982 Summer Average Ozone for Each Hour at Azusa, CA. (Hoggan et al., 1983)

winter at Lennox, Lynwood, Burbank, and Reseda. The highest one-hour value of 27 ppm in 1982 occurred at Lynwood on December 17, 1982. The diurnal distribution of CO follows the morning and evening rush hours. This pollutant is particularly useful in identifying the presence or absence of motor vehicle emissions at each receptor.

- Sulfur Dioxide. SO₂ concentrations are generally low throughout the Basin, except when the monitor encounters a plume. Daytime concentrations are generally higher than nighttime concentrations. This is consistent with SO₂ emissions from elevated sources being injected above the nighttime mixing layer. For the most part, the presence of this pollutant indicates the influence of nearby elevated source emissions. The maximum twenty-four hour average SO₂ concentration in 1982 was 36 ppb at Lennox on December 7.
- Nitrogen Oxides. Highest concentrations were found in 1982 at Los Angeles, West Los Angeles, Lennox, Long Beach, and Whittier. NO₂ concentrations do not show consistent patterns across the Basin, probably owing to the multitude of possible interactions of this pollutant with other pollutants, nearby emissions, and meteorological variables. The maximum hourly average NO₂ concentration in 1982 was 410 ppb measured at Los Angeles on September 3. This followed closely on the maximum ozone concentration which was measured at the same site on the preceding day.
- Total Suspended Particulate Matter. The highest 24 hour TSP levels are detected in an area extending from the eastern San Gabriel Valley, through the Pomona Valley and into the Riverside-San Bernardino area. Seasonal averages vary from location to location, indicating the multiplicity of factors affecting TSP concentrations. The sulfate, nitrate, and lead fractions of TSP provide some insight into the contributors to these pollutant levels. Sulfate typically comprises 7%-13% of TSP and the highest levels are consistently found downwind of major SO₂ emission sources. Highest sulfate levels generally occur during the late summer under conditions of high humidity, while the lowest concentrations are evident in the winter. Nitrate typically comprises 12%-20% of TSP. Highest levels are experienced in the San Bernardino - Riverside area in the summer and fall. Lead concentrations ranged from 0.3% to 1.1% of TSP in 1982 and are decreasing as lead is phased out of use in the motor vehicle fleet (Hoggan et al., 1978). Highest lead levels in 1982 were found in the densely populated areas of Lennox and Lynwood. In 1982, the highest TSP value of 272 µg/m³ occurred at Fontana on July 16 and the highest daily sulfate value of 37.3 µg/m³ occurred at Lennox on December 7, though most other high values were found in the September/October time-frame. The highest annual average nitrate of 21.3 µg/m³ occurred at Riverside and the highest monthly average lead level was 1.7 µg/m³ at Lennox in October. SCAQMD has estimated PM-10 annual averages from 1984 TSP data (Figure 2-7). These averages are likely to exceed 50 µg/m³ at nearly all SOCAB sampling sites, with the sites in the San Bernardino/Riverside areas having the highest values. Measured PM-10 values at seven sites show that Downtown L.A., Rubidoux, Azusa, Burbank, Long Beach and Los Alamitos exceed the new annual PM-10 standard. Only Rubidoux exceeded the new 24 hr PM-10 standard of 150 µg/m³ with a high concentration of 208 µg/m³.

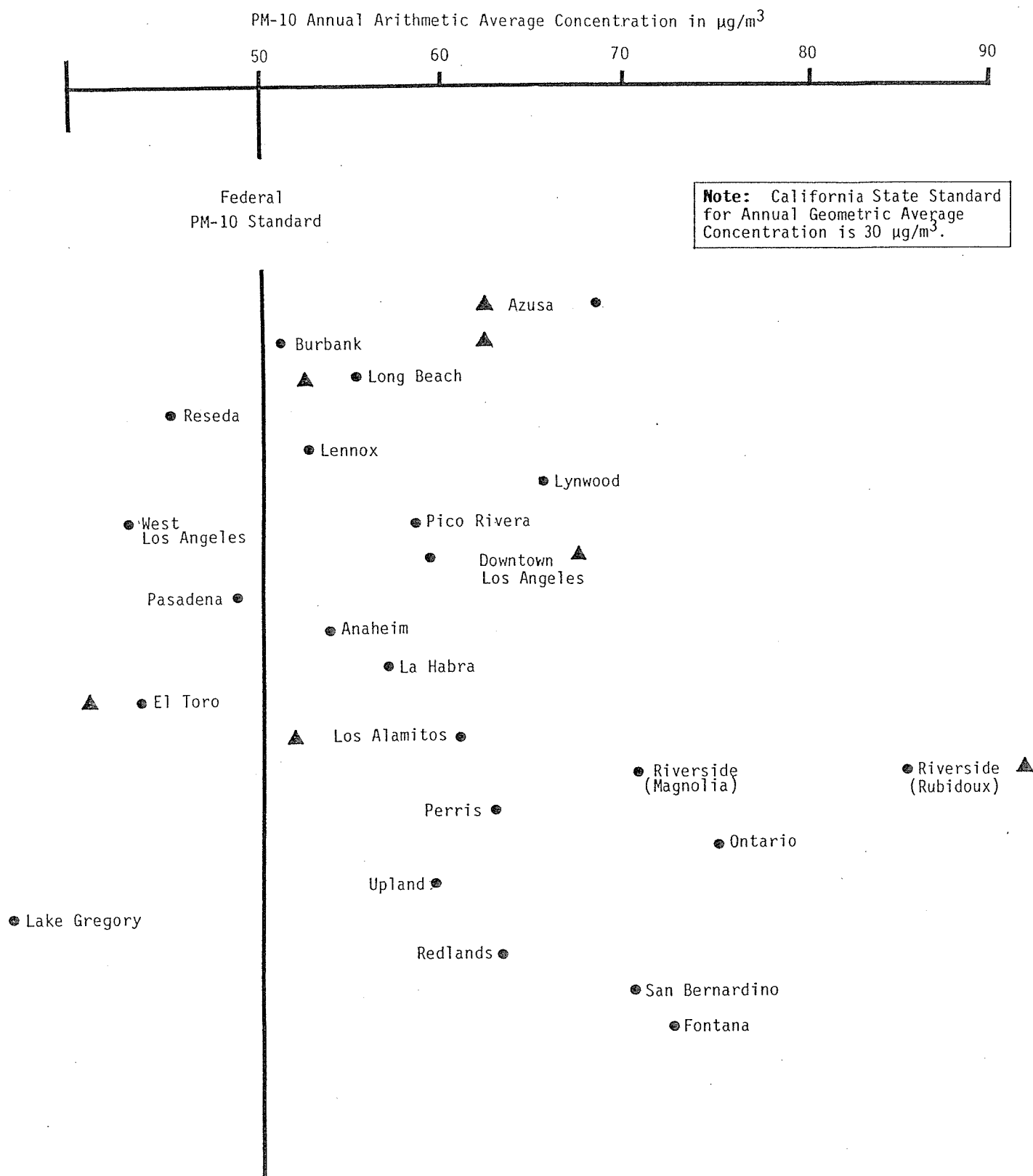


Figure 2-7. Estimated PM-10 Annual Arithmetic Averages (●) from 1984 TSP Data (Based on $\text{TSP} \times 0.59 = \text{PM-10}$) and Measured PM-10 Annual Averages (▲) from October 1984 to October 1985 (personal communication, Art Davidson, SCAQMD, 1985).

While most historical monitoring has focused on O_3 , CO, SO_2 , NO_2 , and TSP owing to their regulation by National Ambient Air Quality Standards, it has been recognized that particulate and gaseous organic material, nitrogenous substances, trace metals, atmospheric mutagens, acid deposition, and visibility are also phenomena of public concern. Both short-term and long-term monitoring programs have been implemented to study these issues. Typical concentrations and ranges for several of these measurements are summarized in Section 3.

A major concern in the interpretation of receptor measurements has been the extent to which these measurements are representative of actual concentrations in the atmosphere. The limitations of measurement technology have repeatedly clouded the interpretation of data used to elucidate cause and effect relationships between variables.

Oxidant measurements taken in the SOGAB prior to 1974 indicated that the major problem areas were confined to the eastern cities in the Basin, and scrutiny of mid-Basin cities, such as Pasadena, was minimized. Pitts et al. (1976) reexamined the oxidant measurements taken between 1955 and 1974 after applying corrections for different calibrations (buffered and unbuffered KI calibrations were converted to an ultraviolet absorption standard) used in Los Angeles County and other counties of the SOGAB. Their re-interpretation of the corrected data concluded that "...oxidant levels do not increase along a west to east axis across the basin [as was previously believed]....they do increase along a southwest to northeast axis across the basin, which roughly matches the orientation of the prevailing onshore sea breezes." Hydrocarbon interferences with the current ultraviolet absorption ozone measurement method must be considered in interpretation of ozone measurements derived from it.

Winer et al. (1974) have quantified the interference of PAN and several other organic nitrates in the chemiluminescent monitoring of NO_2 . Nitroethane and nitric acid were found to interfere, but only semi-quantitative estimates are given by Winer et al. (1974). Grosjean (1983) observed that "On smoggy days... NO_2 can be seriously overestimated if the response of chemiluminescent instruments to PAN and HONO is not taken into account." He found that NO_2 was overestimated by as much as 33%, 56%, and 65% in three different smog episodes. Godden and Lurmann (1983) found that many of their model predictions of NO and NO_2 could easily fall within the range of uncertainties caused by the unknown degree of measurement interference caused by other nitrogenous species. These measurement interferences clearly affect the interpretation of these data and the determination of compliance with standards.

The particle size ranges and chemical composition of routine TSP measurements have been shown to be uncertain. The standard HiVol sampler has a 50% sampling effectiveness between 30 and 50 μm , depending on wind speed and sampler orientation with respect to the wind direction (McFarland et al., 1979). The glass fiber filters used for SOGAB measurements in the recent past yielded higher sulfate and nitrate concentrations than were actually present in the atmosphere (Witz and MacPhee, 1977; Witz and Wendt, 1981; Witz et al., 1982). Spicer (1977) warns that "...some of the extreme particulate nitrate levels recorded in Southern California [in ACHEX] during 1-2 hr afternoon sampling periods may be attributable in part to collection of artifact nitrate." Grosjean (1975) found that the benzene-soluble organic fraction of TSP, which has been measured for years on SOGAB samples, is a variable

fraction of the total organic content which is not relatable to any significant phenomena.

These particle measurement concerns have not been abated by the proposed PM-10 reference method. Watson and Rogers (1985) have evaluated the proposed California Method P for PM-10 mass measurement and have semi-quantified the potential effects of different sampler inlets, filter media, flow measurement and control, sample handling and other environmental variables. Each of these variables has a measurable effect on the mass and chemical species concentrations, though not all of these effects are quantifiable in a specific application. The greatest controversy involves the size-selective properties of PM-10 inlets (Rodes et al., 1985; Wedding et al., 1985; McFarland and Ortiz, 1985; Wedding et al., 1986).

A portion of the difference between ROG/NO_x ratios in ambient air and in the emissions inventory may result from the ambient ROG measurements. Liu (1982) compared measured ROG/NO_x ratios acquired for every day of June, 1981, by three different monitoring methods. Several adjustments were applied to the ROG and NO_x values to account for interferences. These average ratios obtained by the different methods ranged from 1.7 to 41, a range which surely includes the 3.5 ratio yielded by the Basin-wide emissions inventory. The ROG/NO_x ratio of 10.3 which was finally selected for EKMA modeling must, therefore, be used with due consideration of its large uncertainty.

These recognized measurement limitations and their effects on the data interpretation apply to routine measurement methods which have been in place for years. Limitations to several of the measurements proposed for SCAQS in Section 3 are only partially known, or are totally unknown, at this time. Past history suggests that a portion of SCAQS resources should be dedicated to the quantification of these measurement limitations, and that the uncertainties derived from this quantification must be integral to the data interpretation process.

2.3 PAST AIR QUALITY STUDIES IN THE SOUTH COAST AIR BASIN

The South Coast Air Basin has probably been subjected to more air pollution analyses than any other location in the world. Much of the generally applicable and fundamental knowledge regarding emissions, air pollution meteorology, air pollution chemistry, and receptor concentrations has been derived from these studies. The combination of outstanding scientific expertise in California universities, interest from local and national industries located in the SOCAB, community concerns about air quality; and cooperation and financial support from local, state, and federal regulatory agencies has encouraged this high level of productivity. Table 2-4 identifies a fraction of these studies, categorized by specific problem areas. Though this list is far from complete, it conveys the long historical record and the intense scientific interest which are characteristic of air pollution research in the SOCAB.

Most of these studies were of short duration and of small geographical extent. Though they provide evidence of cause-effect relationships among emissions, meteorological, and receptor variables, this evidence is rarely conclusive. These studies have proposed novel measurement, modeling and data interpretation methods, but the modeling efforts have usually had to settle

Table 2-4. Previous Air Quality Related Studies Undertaken in the South Coast Air Basin

EMISSIONS INVENTORY AND CHARACTERIZATION:

ARB (1986)
Cass et al. (1982a)
Chass and George (1960)
Dzubay et al. (1979)
Grisinger et al. (1982)
Huang and Head (1978)
Mayrsohn and Crabtree (1976)
Mayrsohn et al. (1977)
Oliver and Peoples (1985)
Parungo et al. (1980)
Pitts et al. (1984)
Pueschel et al. (1979)
Richards et al. (1976, 1977)
Rodes and Holland (1981)
Rose et al. (1965)
Taback et al. (1979)
Tombach (1982)

METEOROLOGY, WIND FIELDS AND DISPERSION:

Ackerman (1977)
Angell et al. (1975, 1976)
Blumenthal et al. (1978, 1979)
Cass and Shair (1984)
Chang and Norbeck (1983)
Crane et al. (1977)
Drivas and Shair (1974a, 1974b)
Drivas (1975, 1982)
Edinger (1959)
Edinger and Helvey (1961)
Edinger et al. (1972)
Farber et al. (1982b)
Gloria et al. (1974)
Goodin et al. (1979)
Goodin and Lague (1983)
Hanna (1977)
Hidy et al. (1971)
Hinds (1970)
Husar et al. (1977)
Kauper and Niemann (1975, 1977)
Keith and Selik (1977)
Lissaman (1973)
McElroy et al. (1982)
McRae et al. (1981)
Pack and Angell (1963)
Panofsky (1975)
Reible et al. (1982)
Sackinger et al. (1982)
Schultz and Warner (1982)

Table 2-4. (continued)

Shair et al. (1982)
Shettle (1972)
Smith et al. (1972, 1976, 1984)
Smith and Edinger (1984)
Smith and Shair (1983)
Vaughn and Stankunas (1974)
Wakimoto and Wurtele (1984)
White and Husar (1976)
Zak (1982)
Zeldin and Meisel (1977)

MULTICOMPONENT, SIZE-CLASSIFIED AEROSOL MEASUREMENT AND SOURCE APPORTIONMENT:

Cass (1978a)
Cass and McRae (1981, 1983)
Colucci et al. (1969)
Friedlander (1973)
Gartrell and Friedlander (1975)
Giauque et al. (1974, 1979)
Grisinger (1982b)
Hammerle and Pierson (1975)
Heisler et al. (1973)
Hidy (1972)
Hidy and Friedlander (1972)
Hidy et al. (1974, 1975)
Hidy and Mueller (1979)
Ho et al. (1974)
Hoggan et al. (1978)
Huang et al. (1982, 1983)
Husar et al. (1972, 1976)
Ludwig and Robinson (1968)
Lundgren (1971)
MacPhee and Bockian (1967)
Miller et al. (1972)
Mueller et al. (1972)
Neiburger and Wurtele (1949)
Novakov et al. (1972a, 1972b)
Porch and Ellsaesser (1977)
Saltzman et al. (1985)
Stelson and Seinfeld (1981)
Tiao and Hilmer (1978)
Trijonis et al. (1975a)
Volz (1973)
Wadley et al. (1978)
Whitby et al. (1972)
White et al. (1973)
Witz and Wadley (1983)

VISIBILITY:

Alkezweeny and Lockhart (1972)
Appel et al. (1983)
Barone et al. (1978)
Cass (1979)
Charlson et al. (1968, 1969)

Table 2-4. (continued)

Charlson and Pierrard (1969)
Charlson (1972)
Covert et al. (1972)
Ensor et al. (1972)
Noll et al. (1968)
Pratsinis et al. (1984)
Thielke et al. (1972)
Thomas (1962)
Trijonis (1982a, 1982b)
White and Roberts (1977)

SULFATE AND NITRATE MEASUREMENTS AND RELATIONSHIPS TO SOURCES:

Appel et al. (1977a, 1977b, 1978, 1982)
Baboolal and Farber (1982)
Cass (1975, 1978b, 1981)
Grisinger (1982a)
Grosjean (1982a)
Harker et al. (1977)
Heisler et al. (1980)
Henry and Hidy (1979)
Hering and Friedlander (1982)
Novakov et al. (1972a, 1972b)
Richards (1983)
Roberts and Friedlander (1975)
Russell et al. (1983)
Russell (1985)
Russell et al. (1985)
White et al. (1978)
Witz and MacPhee (1977)
Witz and Wendt (1981)
Witz et al. (1982)
Zeldin et al. (1983)

CARBONACEOUS, ORGANIC, HYDROCARBON, AND HALOCARBON MEASUREMENTS
(including toxic organics):

Altshuller and Bellar (1963)
Altshuller and McPherson (1963)
Altshuller et al. (1966)
Appel et al. (1976, 1977a, 1979)
Brenner et al. (1980)
Cass et al. (1982b)
Cronn et al. (1977)
Duval and Friedlander (1981)
Ellis et al. (1984a, 1984b)
Ellis and Novakov (1982)
Gordon et al. (1968)
Gordon and Bryan (1973)
Gordon (1976)
Gray et al. (1985)
Grosjean and Friedlander (1975)
Grosjean et al. (1983)

Table 2-4. (continued)

Grosjean (1975, 1982b, 1984)
Grosjean and Fung (1984)
Gundel and Novakov (1984)
Hester et al. (1974)
Kotin et al. (1954)
Lonneman et al. (1968)
Madar et al. (1952)
Miguel and Friedlander (1978)
Neligan (1962)
Novakov (1982)
Pitts et al. (1981, 1982, 1985)
Rosen et al. (1982)
Schuetzle et al. (1973, 1975)
Singh et al. (1985)
Wolff et al. (1982)

DETERMINISTIC PHOTOCHEMICAL AND AEROSOL MODELS AND APPLICATIONS:

Feigley (1978)
Godden and Lurmann (1983)
Gutfreund et al. (1981)
Haney and Seigneur (1985)
Heisler and Friedlander (1977)
Killus and Whitten (1983)
Liu and Roth (1973)
Liu and Grisinger (1982a, 1982b)
Liu (1982)
Liu et al. (1982)
Lloyd et al. (1979)
Lurmann et al. (1979, 1982)
Martinez (1971a, 1971b)
Martinez et al. (1983)
McRae et al. (1982a, 1982b)
McRae and Seinfeld (1983)
Renzetti and Bryan (1961)
Reynolds (1979)
Reynolds et al. (1973, 1974, 1976, 1978)
Roth (1972)
Roth et al. (1974, 1983a, 1983b)
Seigneur et al. (1981a, 1981b, 1983a, 1983b, 1983c, 1984, 1985)
Sklarew et al. (1972)
Tesché (1983)
Tesché et al. (1983a, 1983b)
Tiao et al. (1976)
Wayne et al. (1971)

PHOTOCHEMICAL MEASUREMENTS AND EMPIRICAL MODELS:

Altshuller et al. (1971)
Aron and Aron (1978b)
Aron (1980)
Bailey (1975)
Calvert (1976a, 1976b)

Table 2-4. (continued)

Caporaletti et al. (1977)
Chang et al. (1980a)
Chock (1982, 1985)
Chock and Levitt (1976)
Chock et al. (1982)
Coyne and Bingham (1977)
Davidson and Cassmassi (1985)
Decker (1972)
Edinger et al. (1972)
Edinger (1973)
Eldon and Trijonis (1977)
Elkus and Wilson (1977)
Estoque (1968)
Evans (1977)
Farber et al. (1982a)
Feigley and Jeffries (1979)
Fontjin et al. (1970)
Grosjean (1982a)
Grosjean et al. (1983)
Grosjean and Fung (1984)
Hamming and Dickinson (1966)
Hanst et al. (1982)
Harris et al. (1982)
Johnson and Singh (1976)
Kok (1983)
Kopczynski et al. (1972)
Lawrence (1972)
Lea (1968)
Levitt and Chock (1976)
Lin (1982)
Littman et al. (1956)
Ludwig et al. (1981, 1983)
McKee (1976)
Merz et al. (1972)
Miller and Ahrens (1970)
Mosher et al. (1970)
Paskind and Kinoshita (1974)
Phadke et al. (1977)
Pitts et al. (1976)
Platt et al. (1980)
Renzetti and Romanovsky (1956)
Reviatt (1978)
Rogers et al. (1956)
Russell et al. (1985)
Schuck et al. (1966)
Severs (1975)
Simmonds et al. (1974)
Spicer (1977)
Spicer et al. (1983)
Stephens (1968, 1969)
Tiao et al. (1975a, 1976)
Tombach (1982)
Trijonis and Eldon (1978)
Trijonis and Mortimer (1982)

Table 2-4. (continued)

Trijonis et al. (1978b)
Tuazon et al. (1978)
Tuazon et al. (1981)
Winer et al. (1983)
Zafonte et al. (1977)

ATMOSPHERIC ACIDITY:

Brewer et al. (1983)
Broadbent et al. (1985)
Ellis et al. (1984c)
Hansen et al. (1982)
Hering et al. (1986a)
Hoffmann et al. (1983)
Hoffmann(1984)
Jacob et al. (1985)
Kawamura and Kaplan (1983, 1986)
Kok (1980)
Liljestrand and Morgan (1978, 1981)
Marsh and Bregman (1984)
Morgan and Liljestrand (1980)
Munger et al. (1983)
Richards et al. (1983a, 1983b, 1985)
Riggan et al.(1985)
Seigneur and Saxeena (1984)
Seigneur et al. (1985)
Shikiya et al. (1984)
Tombach and Pettus (1982)
Waldman et al. (1982)
Waldman (1984)
Waldman et al. (1985)
Walker (1985)
Wall et al. (1984)
Yoong (1981)
Young et al. (1983)
Zeldin and Ellis (1984)

EFFECTS OF EMISSIONS CONTROLS:

Atkinson et al. (1983)
Chock et al. (1981)
Costanza and Seinfeld (1982)
Glasson (1981b)
Hamming et al. (1973)
Kauper and Hopper (1965)
Killus et al. (1981)
Leonard et al. (1976)
Oliver et al. (1983)
Pitts et al. (1983)
Roth et al. (1983a, 1983b)
SCAQMD (1982)

Table 2-4. (continued)

Seigneur et al. (1983c)
Tesche and Burton 1978
Tesche et al. (1984)
Trijonis (1972, 1974, 1983)
Trijonis and Arledge (1975)
Trijonis et al. (1978a)

CARBON MONOXIDE AND PRIMARY NITROGEN DIOXIDE:

Aron and Aron (1978a, 1978b)
Chang et al. (1980b)
Colucci and Begeman (1969)
Hamming et al. (1960)
Horie and Mirabella (1982)
Liu and Goodin (1976)
Neuroth (1979)
Pandolfo and Jacobs (1973)
Pandolfo et al. (1976)
Rogers (1958)
Tiao et al. (1975b)
Trijonis et al. (1975b)
Ulbrich (1968)
Witz and Moore (1981)
Witz et al. (1982)

for whatever data were available. The measurements have rarely been coordinated in such a way that they were compatible with each other or with the models. This brief survey of studies leaves the impression that had these projects been coordinated with one another, and had they been designed around a set of common and inclusive objectives, their value would have been substantially increased.

Important field measurement studies which did involve a degree of this coordination were the Pasadena Aerosol Study (Hidy and Friedlander, 1972), the Aerosol Characterization Experiment (Hidy et al., 1975; Hidy and Mueller, 1979), the Three Dimensional Gradient Study (Blumenthal et al., 1978), the Los Angeles Reactive Pollutant Program (Feigley and Jeffries, 1979), the Los Angeles Catalyst Study (Tiao and Hilmer, 1978), and the Air Quality Maintenance Plan (SCAQMD, 1982). Several of these studies are summarized in Appendix B. Each of these studies involved a planned acquisition of data with the goal of using those data for interpretive purposes. Each study resulted in reports and papers which drew generalized conclusions concerning source-receptor relationships, physical and chemical mechanisms, and the potential effects of emissions changes.

Three of these studies are worthy of further scrutiny in the design of the SCAQS:

- The California Aerosol Characterization Experiment (ACHEX), because it is the predecessor to the SCAQS and it resulted in many of the hypotheses to be tested by the SCAQS.
- The Los Angeles Reactive Pollutant Program (LARPP), because it provided extensive data for model development and testing.
- The Final Air Quality Management Plan Analysis (AQMP), because it serves as the basis for proposed emissions reductions in the SOCAB.

ACHEX was an exploratory study aimed at developing a basic understanding of the sources and compositions of California aerosols. It was successful at describing the size distribution and the major elemental components of the suspended particles. Much was learned about the spatial distribution and composition of the aerosol, and the general sources of particulate matter concentrations were identified. The specific mechanisms for homogeneous and heterogeneous aerosol formation and the composition of the organic component of the aerosol were left as major unresolved issues. The role of water in aerosol formation, composition, and visibility was indicated to be important (Ho et al., 1974), but this role was not defined. The major conclusions of ACHEX were summarized by Hidy and Mueller (1979) as follows:

- the mass concentration of aerosol in California varies widely and is heavily influenced by sulfate, nitrate, and organic carbon formed from gas-phase precursors;
- aerosol concentrations in the eastern part of the SOCAB exhibit marked diurnal variations in concentration and composition. Two-hour average concentrations were substantially higher than 24-hour averages, reaching $450 \mu\text{g}/\text{m}^3$ for mass, $70 \mu\text{g}/\text{m}^3$ for sulfate, $70 \mu\text{g}/\text{m}^3$ for nitrate, and $50 \mu\text{g}/\text{m}^3$ for non-carbonate carbon;

- the multimodal aerosol size distribution was confirmed, with a submicron fraction dominated by aerosol formed from anthropogenic emissions and a supermicron fraction derived from dust and natural sources;
- sulfate, nitrate, and organic species were primarily in the submicron size range. Sulfate was more effective, per unit mass, than any other species in reducing visibility;
- the portion of aerosol attributable to photochemical processes was consistently in the 0.1 to 1.0 μm size range;
- the photochemical mechanism was a major contributor to the formation of sulfate, nitrate, and organic particles. Heterogeneous formation pathways were also inferred to be important;
- ammonia has an important influence on the formation of photochemical aerosol, and these particles may contain a large fraction of water;
- though many sources contribute to the aerosol, sulfate is mainly linked to stationary sources using fuel oil; organic materials result from transportation using gasoline; and nitrates derive from both of these sources;
- more than half of the total suspended particulate material in the SOCAB measured during ACHEX was due to atmospheric chemical reactions. The remaining half was attributed to primary emissions from stationary and transportation sources and background materials such as sea salt and soil dust; and
- the aerosol sources and constituents primarily responsible for visibility reduction varied over the Basin, with sulfate and transportation sources being generally of greatest importance.

ACHEX was a state-of-the-art study for its time. Many of the instruments in common use today were developed for and tested in this study. Since ACHEX, much has been learned via laboratory experiments and field studies regarding the interactions of atmospheric variables, and this knowledge has been incorporated into complex and computationally intensive models which simulate these interactions. In hindsight, and with this additional knowledge, a study to address the issues raised by the above-stated conclusions would be designed quite differently from ACHEX. This hindsight does not detract from the value provided by measurements and data interpretation provided by these researchers more than a decade ago. Of particular note are the large number of publications and fundamental theories which resulted from ACHEX. These results are a direct consequence of the participation of a variety of experts, the open planning process and the free data exchange protocols established at its outset. Several subsequent air quality studies have cost more but were less influential because they neglected these important features.

The Los Angeles Reactive Pollutant Program (LARPP) consisted of airborne meteorological and pollutant sampling of coherent air parcels as they moved along a trajectory. Thirty-five days of sampling were conducted between September and November of 1973. Tetroons and tracer releases were used to locate the positions of air parcels, and instrumented helicopters continuously

measured ozone, nitrogen oxides, total and non-methane hydrocarbons, carbon monoxide and air temperature. Ground-based LIDAR and mobile van measurements were also taken. The data were used in the development and testing of the ELSTAR Photochemical Air Quality Simulation Model (Lloyd et al., 1979). This was one of the first studies which involved industrial (Coordinating Research Council), federal (Environmental Protection Agency and the National Oceanic and Atmospheric Administration) and state (Air Resources Board) sponsors. It provided a model for cooperation among different sponsors to achieve common goals.

While ACHEX and LARPP were primarily research studies which did not focus on pollution control objectives, the AQMP provides a management analysis of more current (1979) emissions and air quality levels with the objective of determining those emissions reductions which are required to reduce air quality concentrations by a certain amount. Three analysis methods applied to routine emissions and ambient data were used by SCAQMD:

- Linear rollback (e.g. Barth, 1970; deNevers and Morris, 1973) was used for CO, SO₂ and NO₂. The total emissions in the Basin are to be reduced by the proportional reduction required of the highest non-background concentration to meet the standard.
- Species fractionation rollback was used for suspended particulate matter. Proportional reductions in Basin-wide primary particulate emissions are prescribed for non-sulfate and non-nitrate fractions of TSP in excess of the ambient standard. Proportional reductions in SO₂ and NO_x emissions are prescribed for the sulfate and nitrate fractions of TSP.
- City-specific EKMA (U.S. EPA, 1981) was applied to 27 station days selected from worst-case situations observed in 1977-1980. Trajectory-specific EKMA was applied to 17 of these cases. Individual back trajectories were plotted for each case and only hourly NO_x and hydrocarbon emissions along those trajectories were considered. Assuming that NO_x emissions will be 23% less in 1987 than they were for 1979, the necessary reductions in Basin-wide hydrocarbon emissions were calculated. Assumptions and sensitivity analyses results are given by SCAQMD (1982) and are too lengthy to repeat here.

The AQMP conclusions are plagued by great uncertainty. There is still controversy concerning whether or not NO₂ emissions reductions will increase or decrease ozone levels (Glasson, 1981a, 1981b; Chock et al., 1981; Pitts et al., 1983; Roth et al., 1983a). Davidson and Cassmassi (1985) provide convincing empirical evidence that shifting emissions schedules may significantly affect ozone concentrations, an option which has not been considered by the AQMP. Given the likelihood that a large fraction of the suspended particle concentrations may be composed of photochemical aerosol, linear rollback may not be an adequate approximation of the effects of emissions on this variable. The large variability in particle composition from site-to-site also calls into question the assumption that Basin-wide emissions reductions will affect the most highly loaded samples in a linear manner. The AQMP presumes a 23% reduction in NO_x emissions by 1987 and a corresponding reduction in suspended particulate matter, ozone, and NO₂ concentrations during that year. The effectiveness of the methods used to arrive at the proposed control measures are amenable to testing.

Contrasting ACHEX and LARPP to the AQMP, it is evident that the research and regulatory needs are complementary. While the regulatory process must continue with the information it has, regardless of the imperfection of that information, it can nevertheless identify where more precise information is needed to make effective decisions. Research efforts can then include, and possibly even focus on, those information needs.

2.4 CONTEMPORARY AND FUTURE AIR QUALITY STUDIES IN THE SOCAB

There is an obvious need for further research to address the cause and effect relationships between emissions, meteorology, and ambient concentrations of precursors and products for ozone and suspended particulate matter. Knowledge of the distributions of other pollutants (such as acidic species and toxic air contaminants) and of their effects on human health, visibility, and materials, is still sparse in the SOCAB. Basic information on the values attained by these observables and their spatial and temporal distributions is needed before these important relationships can be established. The sources, emission rates, and locations of species other than particulate matter, sulfur dioxide, nitrogen oxides, carbon monoxide, and ozone need to be determined. Little is known about PM-10 in the SOCAB and how it is similar to and differs from TSP. With the advent of a new PM-10 standard, and the necessity to create an implementation plan within nine months of promulgation of that standard (Federal Register, 1985), this information becomes even more topical.

Several air quality studies have recently been completed, are currently taking place, or are in the planning stages, which address measurement and modeling issues which are relevant to SCAQS. Some of these have been used in the design of, or made an integral part of, SCAQS.

- The ARB is currently taking samples of benzene, carbon tetrachloride, chloroform, ethylene dibromide, ethylene dichloride, methyl chloroform, perchloroethylene and trichloroethylene gases in Tedlar bags for gas chromatographic analysis. HiVol samples are also being taken with total chromium, lead, manganese and nickel being measured by X-ray fluorescence. The state-wide network includes the Los Angeles, El Monte, Rubidoux, Long Beach, and Upland sites from the SOCAB.
- The SCAQMD and the ARB sponsored a PM-10 sampling network, run by the California Institute of Technology, to measure PM-10 between December 1985 and August 1986. Carbon, ions, and elements have been quantified on the samples. Sampling sites were Burbank, Los Angeles, Lennox, Long Beach, Anaheim, Riverside, and San Nicolas Island. PM-2.5 was measured at the Los Angeles site. Chemical characterizations of particle emissions were also completed. The SCAQMD will apply source and receptor models to these data to estimate source contributions to PM-10.
- Dr. Glen Cass of the California Institute of Technology has recently completed a 15-day measurement program which acquired four-hour aerosol samples between 11 a.m. and 3 p.m. at Pasadena during the summer of 1984. These fine and coarse samples have been chemically characterized and are accompanied by detailed EAA, OPC, nephelometer, RH, T, HNO₃, NH₃, impactor, and SCAQMD gas data. The interpretation of these data is not planned for the near future, owing to lack of sponsorship.

- Project BASIN (Wakimoto and Wurtele, 1984), which was sponsored by the ARB, provided intensive upper air measurements at numerous sites throughout the SOCAB for three days in August of 1984. Mountain wind stations, additional upper air soundings with four-hour resolution, airborne lidar, tracer release, and acoustic sounder measurements were made simultaneously. Though some of these data are being interpreted by scientists at the California Institute of Technology and UCLA, a thorough examination has not been sponsored.
- The Electric Power Research Institute (EPRI) has created a flexible emissions inventorying system covering the entire United States, including the SOCAB (Heisler, 1985). Some of the contents, such as alkaline emissions, nine reactive hydrocarbon classes, and ammonia emissions, are not easily available in other inventories. The inventory system allows rapid updating and regridding for modeling purposes. The current contents are for a base year of 1982, and an update is scheduled for 1987.
- The Southern California Edison Company (SCE) has conducted, and intends to continue, numerous studies in the SOCAB which characterize inorganic and organic components of the aerosol near source dominated as well as photochemically influenced, downwind receptor areas. Over sixty sampling events have been completed at Lennox and Duarte. Inorganic composition has been measured, and detailed organic analyses are being performed on selected samples (Singh et al., 1985).
- SCE released SF₆ from the Ormond Beach Generating Station and took airborne and ground-based tracer and air quality measurements during August, 1985. This study was designed to characterize the chemistry in the plumes of gas and oil powered combustors when coupled with coastal meteorology. The 1985 data are being examined to elucidate the nitrogen chemistry in the plume during periods of elevated ozone concentrations. Additional tracer studies are planned for future years to explore power plant influences on atmospheric acidity. These studies will use soluble tracer species and remote sensing devices, if practical.
- SCE is conducting empirical and objective analyses of air quality and meteorological data to relate aerosol concentrations to meteorological regimes. Source apportionment methods are being developed and tested.
- The Coordinating Research Council (CRC) is sponsoring laboratory and field investigations by researchers at the University of Minnesota to improve size-selective aerosol sampling. Positive and negative biases in the sampling process are being quantified, and steps are being taken to correct them.
- CRC is sponsoring an investigation of the atmospheric chemistry and aerosol-forming potential of aromatic organic substances via experiments in the California Institute of Technology's outdoor smog chamber. These experiments are intended to: (1) identify and quantify the gas-phase reaction products and aerosol molecular composition, (2) measure evolution of aerosol size distributions resulting from atmospheric photo-oxidation of aromatic hydrocarbons in the presence and absence of primary particles, and (3) develop more realistic aromatic gas-phase

photochemical reaction mechanisms for air quality models used in the SOCAB.

- CRC is sponsoring the development of a tunable diode laser to measure NO, NO₂, HNO₃, and HCHO at levels as low as 0.5 ppb. The builder of this instrument, Unisearch Associates, will field test it under polluted conditions typical of those in the SOCAB.
- CRC is sponsoring a project to develop a vehicle evaporative emissions model which estimates emissions from contemporary motor vehicles over a realistic range of operating and ambient temperature conditions. The model will produce more accurate estimates than current methods because it will include diurnal temperature profiles, individual fuel system component temperatures, control system-use pattern interactions, and weathering of tank fuel. This model is applicable to improvements of ROG emission rates in the SOCAB.
- CRC is sponsoring a study of the effects of oxygenates used in gasoline blending on evaporative emissions, with emphasis on ethanol and methanol-gasoline blends. A companion study is intended to determine the effects of fuel volatility, dispensed fuel temperature, and initial tank temperatures, dispensed fuel rate, and vehicle fuel system design on the magnitude of vehicle refueling emissions. Results are applicable to improvements of ROG emission rates in the SOCAB.
- The SCAQMD has recently completed a 1983 emissions inventory update for the SOCAB. The ARB is compiling a 1984 point source inventory and a 1985 planning inventory for the National Acid Precipitation Assessment Program which will include ammonia emissions. The next comprehensive inventory for the SOCAB is scheduled for 1987 with availability by mid-1990. This will be the basis for the SCAQS inventory.
- The Electric Power Research Institute (EPRI) is studying alternatives to the contrast method for determining light extinction in the atmosphere. The assumptions of visibility measurement methods have been examined and alternatives have been developed to eliminate several of the assumptions which are not met in normal situations. Modifications to the integrating nephelometer which minimize the alteration of suspended particles with respect to water, organic content, and size distribution have been explored. The results of these studies can be applied to visibility measurements in the SOCAB.
- EPRI is examining alternatives for the measurement of the liquid water content of suspended particles and constructing a calibration and audit standard for these methods. These methods are applicable to the quantification of liquid water in the SOCAB aerosol.
- EPRI has developed quality assurance and standard operating procedures as part of its regional air quality studies. These procedures have optimized maintenance and performance test schedules and contain appropriate data forms. They are available to be combined with other procedures for the development of a SCAQS procedures manual.

- The ARB sponsored wet and dry deposition measurement networks in the SOCAB. The purpose is to estimate deposition fluxes in the region and to determine the acidity of fog. An estimate of the dry deposition velocities of sulfur and nitrogen species using the profile method (Businger et al., 1971) is included in these measurements.
- The ARB is sponsoring studies of atmospheric mutagens and the role of nitrogenous pollutants in their formation (e.g. Pitts et al., 1981).

These studies and others can help to provide the technical bases for decisions which must be made in the near and distant future. Their results will be even more valuable if they can be coordinated with each other and can be supplemented with additional emissions, meteorological, and air quality measurements which will allow cause-effect relationships to be established.

2.5 DATA NEEDS FOR MODELS

The approach taken in the design of SCAQS has been to start not with the measurements, but with the data interpretation methods. Methods applicable to the air pollution situation in the South Coast Air Basin, including both source and receptor models, have been identified from the references in Table 2-4. These references were reviewed, and, where appropriate, the creators and users of these methods were contacted to determine which measurements would be needed as input data, to determine parameters, to evaluate, and to estimate the uncertainties of these methods. Both research and regulatory applications were considered. Since most data interpretation approaches have been designed around existing data bases, and since they often contain many assumptions or calculational schemes which act as surrogates for non-existent measurements, the recommendations for additional measurements ranged from "nothing" to "everything measured at every point at all times." When reasonable compromises were made, and when past experience with models and data interpretation methods applied to the SOCAB was exploited, several common data needs were identified, irrespective of the data interpretation approach considered.

The most input intensive data interpretation methods are source and receptor models which quantitatively relate ambient concentrations to source emissions. Data which are acquired for these models can also be used for less quantitative data interpretation methods, such as case-studies, statistical summaries, and correlation analysis.

Source models are those which explicitly describe the movement of constituents in the atmosphere and the interactions between them to predict the concentrations of key species at selected receptors which result from source emissions. Receptor models are those which measure numerous variables at selected receptors and infer the source contributions and transport and transformation mechanisms from those data. The data needs of several of these models specific to the South Coast Air Basin are briefly outlined in the following subsections. These models are extremely complex, and volumes have been written to describe them, their assumptions, their data requirements, and the compromises which have been made to accommodate existing data resources. It is not possible for this planning process to summarize all of the information about these models nor to consider the merits of each. This plan will not select "the model" most appropriate for describing the situation in the SOCAB. Model building is an iterative process which attempts to include

those mechanisms and measurements which have the greatest influence on model output. The adequacy of those choices is then tested through focused experiments. The results of those experiments then feed back into the model-building process. The models described here are in evolution even as this is written, and the perceived importance of the data they require will certainly change as new knowledge is gained.

To reiterate: no attempt is made here to prefer one model over another. By polling the modeling community, a common set of measurements has been defined which should be of utility to the future development of several modeling approaches and their ultimate use in making pollution control decisions.

2.5.1 Regression on Principal Components (RPCA)

The RPCA establishes an empirical relationship between atmospheric end-products, such as ozone and constituents of PM-10, by determining rotated eigenvectors of correlations among the causative variables. Linear regressions of the dependent variables on these factors are calculated. RPCA was first applied by Henry and Hidy (1979) to routine air quality data from the South Coast Air Basin, and they found photochemical, relative humidity, and dispersion/stagnation components to have varying influences on ambient sulfate levels. Since that application, several other studies have been published (e.g. Henry and Hidy, 1982; Lioy et al., 1982; Wolff and Korsog, 1985; Malm, 1985; Chow and Spengler, 1985) which show the potential of this method. Chow (1985) provides the most recent summary of these applications and testing of this method.

The RPCA model produces mathematical factors which must be interpreted as physical factors based on the atmospheric variables included in the analysis. These variables need to be selected such that they will be surrogates for the important physical factors. Past applications of RPCA have been limited because these important variables have not always been available.

The important physical factors which are expected to affect oxidant and PM-10 concentrations in the South Coast Air Basin are: (1) primary and precursor emissions of particulate matter, NO₂, reactive hydrocarbons and SO₂, (2) photochemical transformation mechanisms, (3) heterogeneous transformation mechanisms, (4) transport and stagnation, (5) temporal variability of all factors, (6) emissions injection height, and (7) previous day carryover.

The observables which have been deemed important by their users for these RPCA models applied to oxidant and PM-10 concentrations are:

- sequential samples (of four to six hour maximum duration on consecutive days) of size segregated and chemically speciated particulate matter. Important species are geologically-related elements (Al, Si, Fe, Ti), other tracer components (e.g. Pb, Br, V, Ni, Cl, Na, elemental carbon, K), secondary products (e.g. total organic carbon, polar organics, sulfate, nitrate), and in situ liquid water content of the aerosol;
- hourly average oxidant, PAN, speciated reactive hydrocarbons, and NO_x/NO₂ concentrations;

- four to six hourly estimates of mixing depth, ventilation, atmospheric stability, relative humidity, and components of wind direction;
- four to six hourly estimates of fog and cloudwater, when fog exists;
- four to six hourly emission rates in the vicinity of sampling sites, classified by ground-level and elevated injection heights, for primary particles, reactive hydrocarbons, NO_x , and SO_2 . Day of the week variability may be adequate;
- nighttime ozone and PM-10 concentrations off the coast and above the inversion layer; and
- light scattering and extinction measurements which correspond with particle and gas measurements.

The RPCA methods require at least fifty (and preferably over one hundred) sets of measurements which cover the entire range of variability expected to occur. It is not yet known whether or not these methods can be used in a predictive mode nor if they will be able to extract better relationships between causative factors and ozone and PM-10 levels because the data required to test them have not been previously available. The results obtained in the cited studies show promise operating on routine data, however.

Several related models, such as objective analysis methods (e.g. Aron and Aron, 1978a, 1978b; Davidson and Cassmassi, 1985), multiple linear regression (e.g. Pratsinis et al., 1984; White and Roberts, 1977) and time series analysis (e.g. Tiao et al., 1975a, 1975b; Trijonis et al., 1975b) make use of the same data as that required for the RPCA model. Watson et al. (1985) observe that a detailed physical explanation of the processes which are likely to affect the atmospheric end-products, and identification of the variables which are likely to be indicative of those processes, is a pre-requisite for a RPCA application. Though Watson et al. (1985) provide such an explanation for factors affecting fine particulate concentrations in the San Joaquin Valley, their analysis is not complete enough to cover the more complex situation in the SOCAB.

2.5.2 Chemical Mass Balance Receptor Model

The chemical mass balance (CMB) receptor model (e.g. Friedlander, 1973) has been used as the basis for control strategies related to total suspended particulate matter (e.g. Cooper et al., 1979). However, the major contributors in these previous applications have been related to primary emitters. Since previous measurements have shown that major contributors to TSP in the SOCAB are of secondary origin, this model may not be directly applicable to the apportionment of these aerosols to sources. Nevertheless, this model is being incorporated into EPA's PM-10 assessment guidelines (personal communication, Tom Pace, U.S. EPA Office of Air Quality Planning and Standards, August, 1985) and has been shown (Watson, 1979) to put an upper limit on the secondary aerosol contribution and to apportion some of the precursors (Mayrsohn and Crabtree, 1976; Tombach, 1982; Feigley and Jeffries, 1979) of secondary aerosol to their sources. If the fractionation among species from various sources as a result of transport and transformation can be measured (e.g. Houck et al., 1982) or estimated (e.g. Duval and Friedlander, 1981), then the

CMB might be an appropriate method for apportioning PM-10, and possibly the precursors of ozone, to their sources.

The CMB model consists of solutions to a set of equations which describe receptor concentrations of selected constituents as linear sums of the fraction of each constituent in source emissions times the total mass contribution of that source to the receptor. The receptor concentrations and source compositions are given to the model and the contribution from each source to each atmospheric constituent is calculated. Chow (1985) provides the most recent compilation of past applications while Watson (1979) presents the model assumptions and testing results. Other test results are reported by Currie et al. (1984) and Dzubay et al. (1984).

A recent evaluation of this model sponsored by the Electric Power Research Institute (Harold Javitz, SRI International, personal communication, September, 1985) concludes that although the CMB formulation is adequate for accurately determining many source contributions, even aggregate secondary contributions and the contributions to their precursors, this adequacy is extremely sensitive to the available observables and their random variability. The accuracy of current applications has been controlled more by the inadequacy of source profile measurements than by ambient measurements. There is no set of common source profile measurements in which all emitted species are characterized for all important sources. Chow (1985) and Edgerton (1985) have recently shown the value of including gaseous as well as particulate species measured in both the source and receptor samples. This increases the accuracy and precision of source apportionment and allows the gaseous species to be apportioned to their emitters. Very few current source profile measurements include the gaseous as well as particulate chemical constituents.

Although the CMB model can be applied to single samples of any duration, samples taken over shorter time periods provide more precise results in that they allow a better definition of contributing sources and a more accurate estimate of fractionation factors.

The important input data needs for the chemical mass balance model are:

- receptor particle measurements of key elements (Al, Si, Pb, Br, K, Cl, Na, V, Ni, Fe), ions (SO_4^{+} , NO_3^{-} , NH_4^{+}), organic and inorganic carbon, speciated organic materials, and individual particle characteristics in 0 to 2.5 and 0 or 2.5 to 10 μm size ranges;
- receptor gas measurements of NO_x , SO_2 , CO, reactive and nonreactive hydrocarbons;
- source profiles for power plant, motor vehicle, refinery, resuspended dust, and marine aerosol which include gaseous and particulate observables specified above for all sources; and
- estimates of fractionation factors (after Stafford and Liljestrang, 1984) between source and receptor.

2.5.3 Photochemical and Aerosol Models

Many grid and trajectory models have been proposed for describing the relationships between emissions and receptor concentrations. Each of these involves transport and transformation mechanisms. Godden and Lurmann (1983), McRae et al. (1982a), Killus et al. (1985), and U.S. EPA (1981) describe photochemical mechanisms which have been incorporated into deterministic modeling packages. Each of these models has been applied to the June 26 and 27, 1984 smog episode and the O_3 , NO , and NO_2 concentrations have been compared with those at downwind monitoring stations. Though these "model validation" studies are not strictly comparable, the comparisons of model results and ambient measurements are qualitatively equivalent, regardless of the model used. A model/model comparison is not justified based on the individual reports, however, because these applications were never coordinated in such a way that objective performance measures could be calculated. While much emphasis has been placed on model performance (i.e. a one-to-one match in model end-product with a corresponding measurement in place and time), little emphasis has been placed on model diagnostics (i.e. the comparison of intermediate model calculations with measurements of reactive species and independent measurements of transport variables in space and time). Sensitivity and uncertainty analyses (e.g. Seigneur et al., 1981a; Tilden and Seinfeld, 1982) have shown that model end-product values vary substantially, even with small variations in selected input data. The sensitivity of intermediate calculations, and the extent to which input errors compound upon each other, have not yet been compared to real measurements outside of a smog chamber.

Work is underway to better represent other aerosol formation processes in these models (Seigneur et al., 1985, Russell et al., 1983). The ultimate goal is to produce comprehensive treatments which can estimate receptor concentrations of PM_{10} , ozone, and other constituents with specified accuracy and precision. These are currently the only types of models which are capable of estimating the effects of a hypothetical change in emissions on air quality. Receptor models can only be used when they are applied before and after such an emissions reduction has taken place.

These models require precise definitions of wind fields, initial values of pollutant and precursor concentrations of the atmospheric constituents, reaction rates, vertical and horizontal fluxes into and out of the volume being modeled, temporal and spatial distributions of gaseous and particulate precursor and primary emissions, and deposition rates at surfaces. It is technically impossible to measure all of these variables with the spatial and temporal resolution required of the models; therefore, simplifying assumptions regarding their values are used to estimate them.

The most important measurements which are not currently being made, but which are feasible, are the following:

- emission rates with a three hour minimum time resolution. The photochemical precursors, NO_x , and speciated hydrocarbons, are the most important species. These are needed as input data for photochemical and aerosol models;

- improved speciation for both gaseous and particulate emissions. The same types of measurements should be made on all major source types and should include elements, ions, organic and inorganic carbon, sulfur dioxide, nitrogen oxides, ammonia, carbon monoxide, speciated gaseous and particulate organic species. Exhaust gases should be cooled, diluted and preferably aged prior to sample collection to approximate their compositions in the environment. Aggregate samples of area sources (e.g. motor vehicle emissions) are preferable to measurements of single sources. These measurements should be sufficient to determine ROG/NO_x ratios for all sources. These speciations are needed both as input data for source models and for receptor models. Ammonia emission rates are also needed for aerosol models;
- accurate wind fields which account for the complex meteorological phenomena described earlier. These are critical to the establishment of effective cause-effect relationships between emissions and receptor concentrations. Additional locations and more frequent upper air measurements are needed to supplement and verify surface measurements;
- boundary and initial concentrations of oxidant and particulate species, and their precursors. These are needed to determine their evolution over a period of time. Of critical importance are the concentrations above the mixed layer during nighttime and morning periods. Concentrations over the ocean are required, and these may be at levels lower than those detected by conventional instruments which have been used previously. Hydrocarbon speciation and free radical concentrations are also needed at various sites to serve as initial concentrations and to verify model predictions throughout a simulated event; and
- intermediate reaction products. These are required to verify that chemical mechanisms are reproducing the multitude of chemical constituents which are actually observed during an episode.

2.6 SUMMARY

It is impossible to do justice to the wealth of information available regarding air quality in the South Coast Air Basin in a survey of this type. The emphasis here has been placed on learning from the past in order to gain in the future. The subsequent parts of this program plan have been influenced by these lessons, which can be summarized as follows.

- The value of simultaneous measurements of emissions, transport, transformation and receptor variables is far greater than the value of any of these measurements acquired at disparate places and times, and the cost effectiveness of simultaneous data collection exceeds that for separate studies.
- The physical and chemical understanding of the atmospheric processes affecting pollutant concentrations in the SOCAB is sufficient to define the observables which need to be measured, their averaging times, and the characteristics of episodes which are conducive to high pollutant concentrations.

- Measurement technology is capable of determining the values of most observables, but each measurement method has a set of assumptions which must be met. Provisions must be made to test those assumptions for each measurement period, and to consider deviations from them in the data interpretation process.
- Potential data interpretation methods, including models, must be identified prior to taking the first measurement and their data requirements must be specified. These requirements include testing as well as input data.

3. MEASUREMENT APPROACH

This section describes the planned SCAQS field measurements. The measurement approach has been revised since the last version of the program plan (Blumenthal et al., 1986). Recommendations from participants, sponsors, and several working groups which were set up to design and review specific aspects of the study have been taken into account in the revised design. The planning activities, the role of the Field Manager, the measurement recommendations of the modeling community, and the rationale for selection of the sampling periods are summarized in Sections 3.1 through 3.3. The study includes a series of "core" measurements along with several complementary studies which address specific issues. The core measurements are described in Sections 3.4 through 3.7. Most of the special studies are described in Section 3.8; however, some of them are included in the list of A-site measurements in Section 3.4.

3.1 PLANNING AND MANAGEMENT

3.1.1 Planning Activities

The suggested program plan prepared in June, 1986 (Blumenthal et al., 1986) has been revised based upon three types of input. First, the suggested plan was widely distributed to the technical community and potential participants for their review and comment. Second, Emissions, Meteorology, and Model Working Groups were formed to review the plan and to recommend specific measurements and data collection activities which would meet the needs of the analysts and modelers who will use the data. Finally, the sponsors negotiated work statements with the participants who will perform the measurements listed in this section.

In light of the finite resources of the sponsors and limited technical feasibility of some of the measurements, compromises were made to arrive at the consensus program plan presented here. The final design process was an iterative effort with continual review by the Working Groups and the sponsors. Numerous meetings were held, and all points of controversy were pursued until a consensus was reached between the measurements participants, the working groups, and the sponsors. The detailed recommendations of the working groups are discussed in the remaining parts of Section 3 and are reflected in the study design.

3.1.2 Field Management

The SCAQS field program will be coordinated by a Field Manager who will perform the following tasks:

- determine the power, space, and logistical needs of all field participants;
- arrange for access to the AQMD sites to be used during SCAQS;
- arrange for additional power and other necessary facilities;

- coordinate the activities of all measurement personnel and provide support as necessary. The sites will be operated by a contractor whose activities will be coordinated by the field manager;
- prepare the field measurement protocols;
- disseminate daily meteorological forecasts and sampling decisions to the participants;
- coordinate the distribution, exposure, labeling, and transportation to the laboratory of all routinely collected samples; and
- document field activities for progress reports.

3.2 MODEL WORKING GROUP RECOMMENDATIONS

To aid in the planning process, a Model Working Group was established. Members of the Model Working Group are listed in Appendix A. The sampling sites and specific measurements suggested for SCAQS in the Suggested Program Plan (Blumenthal et al., 1986) were based on initial discussions with potential sponsors, participants, and modelers. To assure that the measurements will meet future model and data analysis needs, some preliminary modeling and data analysis activities were performed by members of the Model Working Group to analyze the adequacy of the various components of the SCAQS measurement plan. The results of these activities were considered in this revision to the program plan.

The general question underlying the Model Working Group's analysis is -- If the SCAQS program were completed and the planned measurements were all successful, how would the data be used to test, evaluate and improve air quality models? Conversely, can the proposed measurements be planned such that the optimal amount of information can be obtained to meet the goals of the study.

The analyses performed by the Model Working Group and their recommendations are presented in a MWG report (Seinfeld et al., 1986) and are summarized below.

3.2.1 Gas-Phase Chemical Measurements

Lurmann et al. (1986) carried out an extensive set of chemical mechanism trajectory calculations in an effort to determine those gaseous species measurements that would aid most in elucidating ROG/NO_x/ozone chemical reaction mechanisms. The conclusions arising from this study relevant to the choice of gas-phase measurements are as follows:

- Reactive Hydrocarbon Measurements: The total level and speciation of reactive hydrocarbons have the strongest influence on predicted ozone species. Therefore, it is extremely important that reactive hydrocarbons be measured as planned (see Section 3.4). In addition to gas chromatography measurements, it is recommended that occasional gas chromatograph/mass spectrometer measurements be made to ensure proper identification of the peaks.

- Free Radical Measurements: The Working Group studied in detail the question of which free radicals provide the most opportunity for evaluating our knowledge of the gas-phase chemistry and for discriminating among rival chemical reaction mechanisms. The conclusion arising from the studies is that measurements of peroxy radicals, namely, HO_2 and RO_2 , will provide the greatest amount of information concerning the detailed behavior of chemical mechanisms. Separate measurements of HO_2 and RO_2 would be best, but, if that is not possible, measurement of the sum of HO_2 and RO_2 is also of value. Although hydroxyl radical measurements have been proposed, these measurements are most useful in assessing the overall OH level in comparison with predicted levels. They will not allow differentiation of chemical reaction mechanisms since all mechanisms predict essentially the same OH levels.
- Hydrogen Peroxide Measurements: Hydrogen peroxide is a very sensitive indicator of HO_2 levels and is an important species in its own right. Measurements of H_2O_2 are viewed as essential.
- Formic Acid: Formic acid measurements would provide an important test of our understanding of the olefinic portion of reaction mechanisms. These measurements are encouraged.

The Working Group places a substantially lower priority on continuous nitric acid measurements than those listed above. However, as noted below, nitric acid measurements on the same time resolution as the aerosol nitrate and ammonia gas-phase measurements are essential.

In commenting additionally on the hydrocarbon measurements, the Working Group deems it very important to determine the total hydrocarbon cloud surrounding the Basin, namely, how far out and how high it extends. The question of marker compounds was discussed. It is important that the incoming air from the ocean be characterized with respect to its hydrocarbon level and composition.

Pilinis and Seinfeld (1986) used an air quality aerosol model to determine the sensitivity of the size and chemical composition of a simulated receptor aerosol to various input variables. Their studies result in the following recommended gas-phase measurements:

- SO_2 Aloft: Since more than 50% of the SO_2 is emitted aloft from various point sources, upper-air SO_2 concentration measurements are very important. Of special importance is the concentration of SO_2 above the mixed layer overnight. This can be fumigated to the ground when the inversion layer grows the next day.
- NH_3 and Nitric Acid: Aerosol nitrate and nitric acid exist in equilibrium, and the aerosol nitrate concentration is dependent on the amount of ammonia present in the atmosphere. An increase of only 10% in the amount of ammonia can result in a substantial increase in NH_4NO_3 in the aerosol phase.
- Temperature and Relative Humidity: Perturbations of 5 degrees C and 30% RH are common during the day in the Basin. Such perturbations can result

in substantial changes in aerosol mass and physical state, which affect the composition and size distribution of the aerosol.

3.2.2 Aerosol Measurements

Pilinis and Seinfeld (1986) used an air quality aerosol model to determine the sensitivity of the size and chemical composition of a simulated receptor aerosol to various input variables. Their studies result in the following recommendations for the general aerosol measurements:

- Organic and Inorganic Aerosol Concentrations: Coarse (by difference) and fine aerosol loadings should be measured on a routine basis for both organics and inorganics.
- Particle Absorption and Scattering: Both integrating plate particle absorption and particle scattering by nephelometer should be measured on a routine basis.
- Time Resolution: The routine aerosol measurements at the B-sites should be every four hours during the daytime, and could be longer at night. The four-hour samples should start at 0600 local time to coincide with the morning rush hour.

For the impactors and aerosol physical measurements, they recommend the following:

- Impactors: A minimum of five size cuts are needed for aerosol size and chemical composition modeling. Organic and inorganic size distributions are needed. Specifically, elemental and organic carbon size distributions should be measured using the MOUDI impactor; inorganic ion size distributions should be made with the Berner impactor.
- Time Resolution: Twelve-hour averaging for inorganic ion impactor measurements are of little value for aerosol modeling, since temperature and relative humidity changes over 12 hours will change the aerosol substantially. Also, organic aerosol concentrations probably peak on short time scales, just like ozone concentrations. Thus, these measurements should be as short as possible, probably four hours long during the daytime and six hours at night. A 12-hour nighttime sample could replace the two 6-hour samples if necessary.
- Impactor Sites: Aerosol size-composition distributions for inorganic ions are needed for aerosol modeling at both the beginning and the end of a trajectory. However, it is unlikely that a given trajectory will begin at Long Beach and end at Claremont. Also, the predicted aerosol mass and chemical composition are significantly different when the trajectory is Long Beach-to-Claremont, versus Anaheim-to-Rubidoux. At least two receptor measurement sites are needed in order to allow interpolation where data are not available. Thus, the Berner impactor measurements should be made at more than the two A-sites; Rubidoux is the recommended third site. Also, the two receptor sites will allow a comparison between the aerosol at an ammonia-poor site (Claremont) and an ammonia-rich site (Rubidoux).

- Aerosol Physical Measurements: Detailed aerosol size distributions are needed for aerosol modeling. A combination of an electrical mobility analyzer, an optical particle counter, and a large-particle counter could supply hourly-averaged size-distribution data. It is most critical that these measurements be made at the source site (Long Beach) and the two receptor sites (Claremont and Rubidoux). These measurements could be supplemented with a classifier/CNC at the receptor sites.

3.2.3 Meteorological Measurements

Kessler et al. (1986) carried out a number of wind field generation calculations for the South Coast Air Basin. The first conclusion from those studies is that one cannot construct a good three-dimensional wind field from surface measurements alone; upper air data are crucial. The second major conclusion is that the current surface network proposed for SCAQS is adequate for generating a surface level wind field. With approximately six upper air measurements, the question is -- Where should these be made and how frequently? It was generally agreed that measurements in the interior of the SOCAB will be more useful than measurements in the outlying areas, for the purposes of data analysis.

3.2.4 Emissions Inventory

The ROG speciation of the inventory should be consistent with the two types of chemical mechanisms used today in photochemical modeling. The recommended compound classes for the two types of mechanisms are:

<u>Surrogate Species Mechanisms</u>	<u>Carbon Bond Mechanism</u>
C4-C5 Alkanes	Paraffinic Bonds
>C5 Alkanes	
Ethene	Ethene
Terminal Alkenes	Olefinic Bonds
Internal Alkenes	
Mono-alkylbenzenes	Mono-alkylbenzene Bonds
Di-alkylbenzenes	Di-alkylbenzene Bonds
Tri-alkylbenzenes	
Formaldehyde	Formaldehyde
Acetaldehyde	
Other Carbonyls	Other Carbonyls
Nonreactive	Nonreactive

The Systems Applications, Inc. Urban Airshed Model (UAM) has been applied extensively in the South Coast Air Basin utilizing a horizontal grid resolution of 5 km (Reynolds et al., 1973; Roth et al., 1984). Seigneur et al. (1981) demonstrated a significant deterioration in model performance in the SOCAB when the grid size was increased to 10 km; based on this result, 5 km should be considered to be the minimum resolution required for effective application of the UAM in this region.

The standard temporal resolution of UAM emissions inventories has been one hour. In general, data on point and mobile source emissions can be obtained with this temporal resolution. Frequently, only yearly rates are

available for area sources; in this case, day-to-day and hourly variations must be either inferred or ignored. Seigneur et al. (1981) indicate relative insensitivity of the UAM to detailed diurnal resolution of area source emissions. However, the use of yearly information on area sources can introduce significant uncertainty into UAM predictions in cases where seasonal variability in area source emissions is significant. Thus, an effort should be made to obtain daily, monthly or seasonal resolution of area source emissions.

Various UAM applications have indicated that emissions uncertainties of the order of 5-10% would not have significant effects on peak ozone concentrations predicted by the model, while uncertainties of the order of 30-50% in emission rates may produce major uncertainties in predicted ozone peaks.

Primary aerosol particles, emitted directly into the atmosphere, consist principally of elemental and organic carbon and various inorganic species. The primary carbonaceous particles will presumably be chemically inert with respect to the inorganic system; their presence, though, does affect the predicted aerosol size distribution, as well as the total suspended mass. Due to this importance, the aerosol emissions inventory should include both PM-2.5 and PM-10 size fractions for aerosol mass and for both elemental and organic carbon.

3.3 SELECTION OF STUDY PERIODS

The two study periods have been chosen to be representative of the worst oxidant and aerosol periods in the South Coast Air Basin. In addition, these periods will document three substantially different types of pollutant conditions.

The first study period will take place from June 15 to July 26, 1987. The first part of this summer period is typically a period of high humidity in the South Coast Air Basin and should be a period which favors heterogeneous aerosol formation. During June, the percentages of days with low morning stratus clouds and poor afternoon visibility in the inland areas are the highest of any month, as indicated in Table 3-1. The highest average suspended particulate concentrations in the Basin typically occur in June, July, and December. The second half of the summer study period typically experiences the highest concentrations of photochemical pollutants of the year. High ozone concentrations generally occur in the Basin when the 850 mb temperature is greater than 20 °C. Figure 3-1 indicates that July includes the most consistently high 850 mb temperatures of the summer. Figure 3-2 indicates that July also experiences consistently high maximum ozone concentrations. During mid-to-late July, the inland visibility is consistently low (Table 3-1), and there are stratus clouds along the coast about 1/3 of the time. Inland stratus is much less common. Thus, the summer sampling period should produce periods of primarily homogeneous chemistry as well as periods when coastal pollutants interact with water droplets which subsequently dry out as they travel inland. Twelve intensive sampling days, covering episodes of two or three days duration, will be selected from this six-week period on a forecast basis as described in Section 3.7.

Table 3-1. Percentage of Days for 1978-83 with Early Morning Clouds and Low Afternoon Visibility.

	Ceiling (0800 PST)		Visibility (1400 PST)	
	LAX ≤1800 ft.	ONT ≤1000 ft.	LAX ≤6 miles	ONT ≤6 miles
May 1 - 15	19%	16%	12%	49%
16 - 31	37	27	20	65
June 1 - 15	40	25	36	75
16 - 30	33	21	12	63
July 1 - 15	27	8	17	44
16 - 31	33	9	33	71
August 1 - 15	40	13	27	55
16 - 31	32	8	18	53
Sept 1 - 15	15	12	31	49
16 - 30	21	3	20	41
Oct 1 - 15	36	12	37	51
16 - 31	18	9	33	44

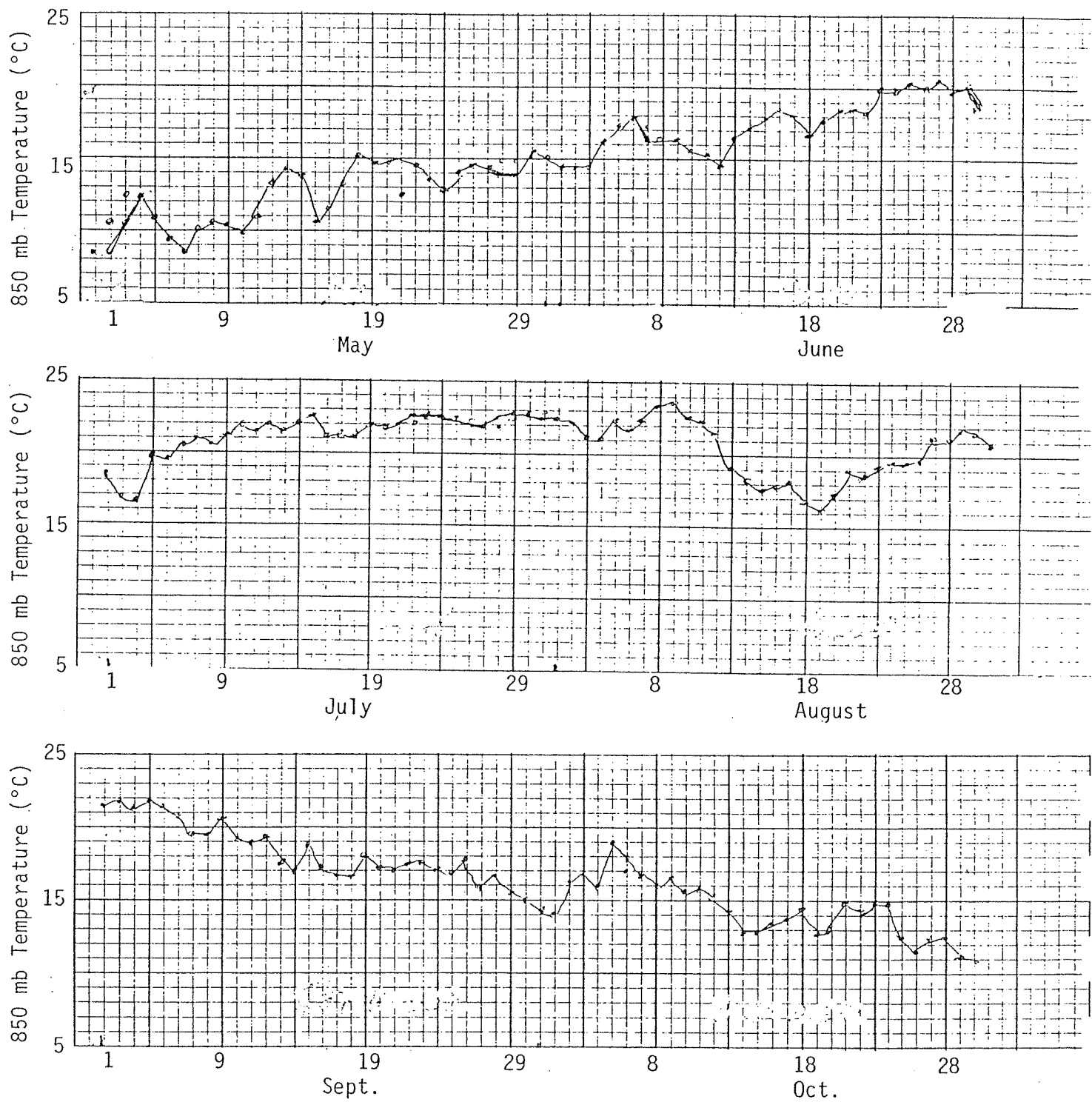


Figure 3-1. Daily Average 850 mb Temperature (Los Angeles, 1976-84).

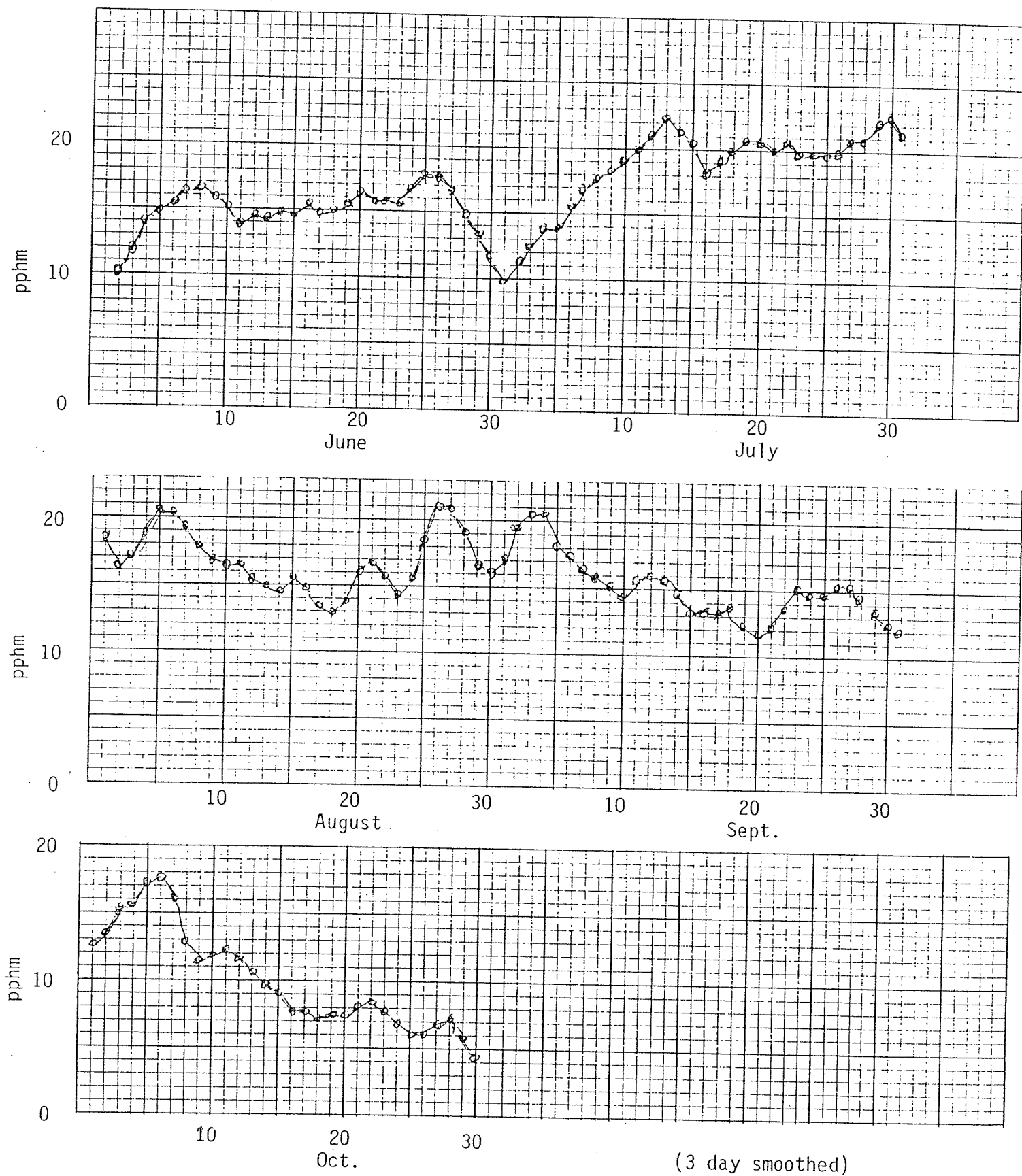


Figure 3-2. Maximum Ozone at Pomona. (Average of 1978-83.)

The second study period will take place from November 16 to December 13, 1987. This period was chosen to measure late fall stagnation conditions. NO₂ and CO episodes tend to occur at this time, and low inversions and cool temperatures tend to favor the accumulation of primary pollutants. The average daily maximum NO₂ concentrations for September-December in the SOCAB for a six-year period are plotted in Figure 3-3. This sampling period is early enough to avoid the probability of substantial numbers of down days due to winter storms. Six intensive sampling days covering episodes of two or three days duration will be selected on a forecast basis as described in Section 3.7.

The lengths of these sampling periods minimize the probability of missing synoptic conditions of interest due to periods of unusual weather. The choice of the study periods was reviewed and endorsed by the staff of the SCAQMD (Liu, 1986).

3.4 SURFACE AIR QUALITY MEASUREMENTS

3.4.1 Measurement Site Locations

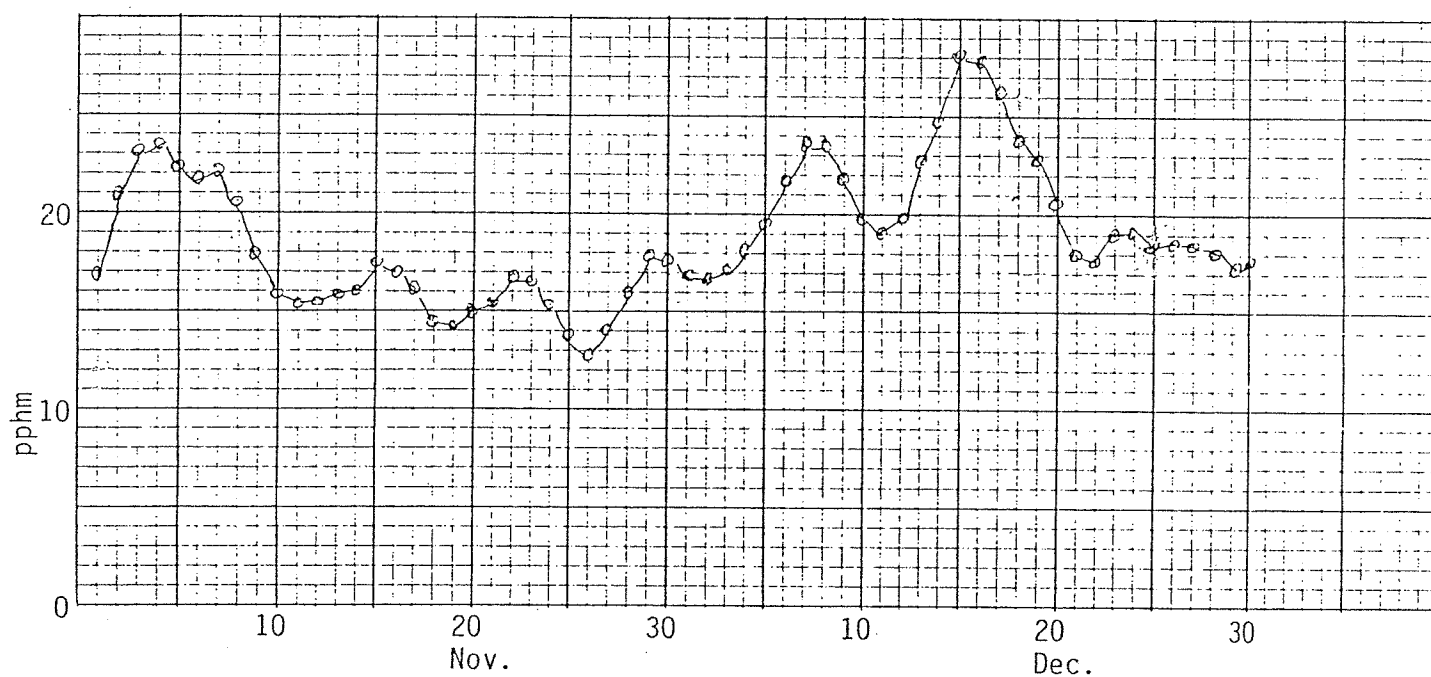
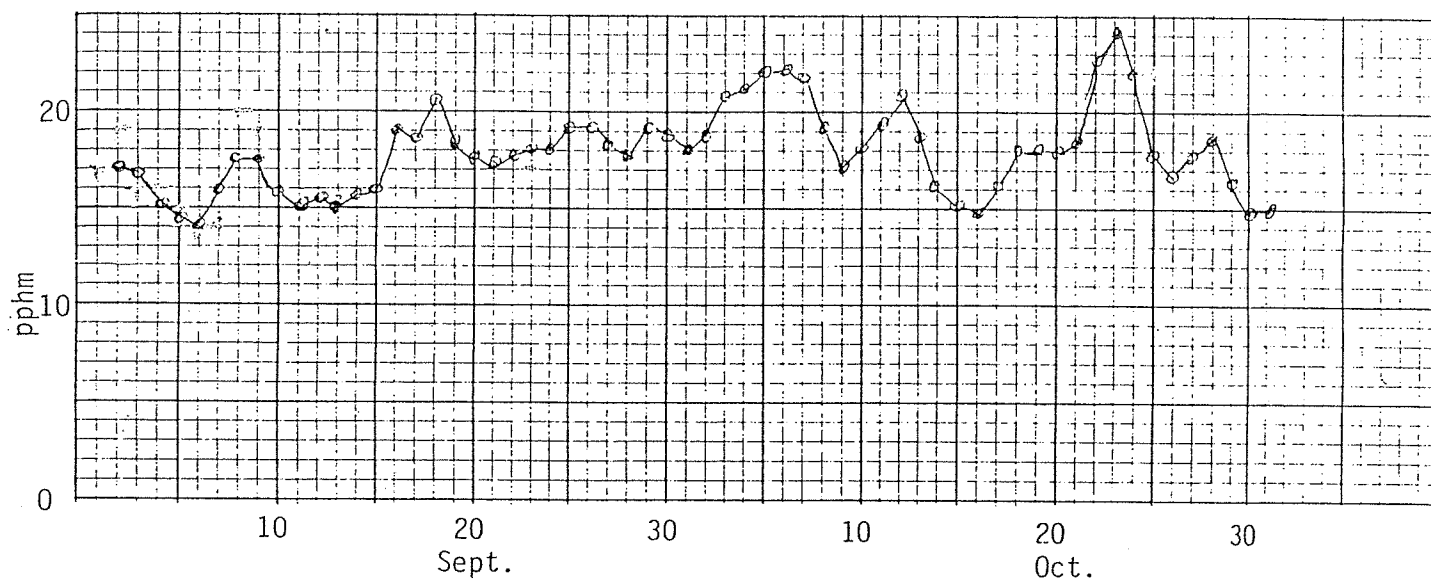
The study region includes the South Coast Air Quality Management District (SCAQMD), the upwind portions of Ventura County, and adjacent offshore regions. Three types of pollutant measurement sites, identified as A-, B-, and C-sites, will be operated in this region. The characteristics of the sites are described below. The C-site locations are shown in Figure 2-1 and identified in Table 2-3; the B- and A-site locations are shown in Figure 3-4.

C-Sites

C-sites include the existing monitoring stations of the SCAQMD, the Ventura County Air Pollution Control District, and other stations at which air quality data are routinely collected and reported. Data from these sites will be routinely acquired and archived by the Districts and integrated into the SCAQS data base after the measurement program.

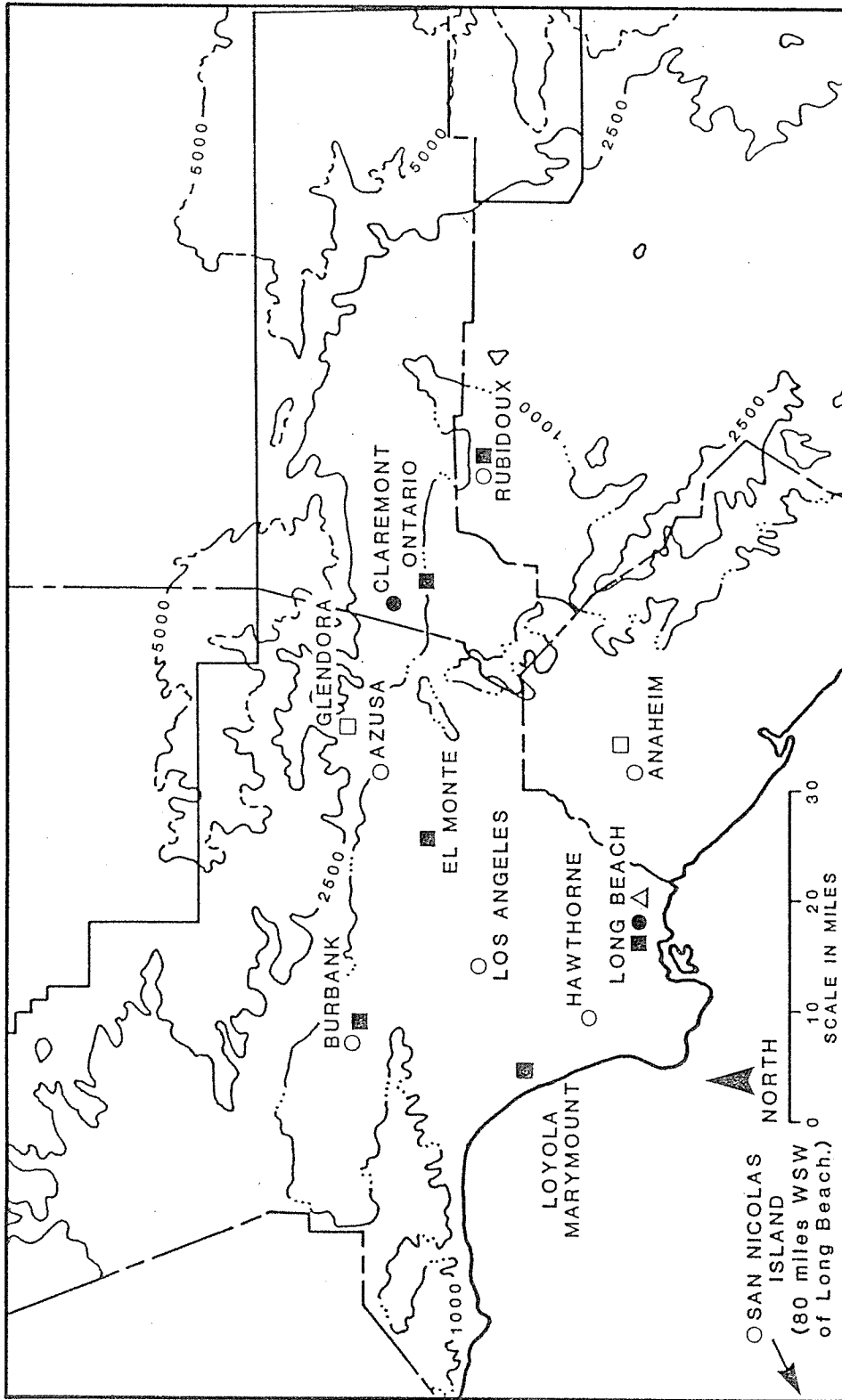
B-Sites

B-sites are located along typical SOCAB air trajectories and acquire more measurements with greater frequency than the C-sites. These enhanced measurements will be made on the intensive sampling days selected by the forecast strategy described in Section 3.7. During the summer sampling period, the Anaheim, Azusa, Burbank, Downtown Los Angeles, Hawthorne, and Rubidoux sites are collocated with C-sites and a regional-scale background B-site is located at San Nicolas Island. The Long Beach and Claremont B-sites are also A-sites. The Claremont, Long Beach, and Rubidoux sites are termed B+ sites because their measurements are further enhanced with high-resolution particle size and chemistry monitors. During the fall sampling period, the number of B-sites will be reduced to five located at Anaheim, Claremont, Downtown Los Angeles, Hawthorne, and Long Beach. Long Beach and Claremont will be B+ sites for this fall period.



(smoothed 3-day mean
of daily maxima)

Figure 3-3. Maximum NO₂ - South Coast Air Basin. (Average of 1978-83.)



Southern California Air Quality Study.

Legend:

- - Type A Sites
- - Type B Sites
- △ - Doppler Acoustic Sounder
- - Rawinsondes
- - Airsondes

Upper Air Meteorological Stations:

Figure 3-4. Air Quality and Upper Air Meteorology Monitoring Sites for SCAQS (Contours in feet).

A-Sites

A-sites will be the base of operations for selected intensive measurements, special experiments, and individual investigators. Long Beach and Claremont are the A-sites for the summer sampling period. These sites represent source and receptor regions respectively. Only the Long Beach source-oriented site is a A-site during the fall sampling period. A-site instruments are operated primarily on intensive study days, but some researchers will operate their equipment continuously.

3.4.2 SCAQS Air Quality Measurements and Measurement Methods

The observables to be measured at the A-, B-, and C-sites, the averaging times, and measurement frequencies are presented in this section.

C-Site Measurements

The C-site measurements consist of those air quality and meteorological variables which are normally measured by the Air Quality Management Districts. Table 3-2 summarizes these measurements, and the specific measurements at each station are identified in Table 2-3. The measurements methods and procedures at the C-sites are already in place and are quality assured by the Districts and the ARB on a regular basis. These data will be extracted from the Districts' data base for the SCAQS summer and fall sampling periods and integrated with the rest of the SCAQS measurements.

B-Site Measurements

All of the C-site measurements will also be made at B-sites throughout the summer and fall periods. The measurements to be made at the B-sites are identified in Tables 3-3a through 3-3f. The continuous measurements will be made on all days during the study period. The other measurements will be made only on the intensive sampling days. The measurement methods were selected after extensive evaluation of different alternatives with respect to reliability, sensitivity, cost, availability, and compatibility with existing measurements. Only brief reasons for selecting each method are given in the tables, since the entire selection rationale is too involved for presentation in this program plan. Table 3-3a also includes estimates of the ambient concentration, lower quantifiable limit, and precision for each measurement. In all cases the lower quantifiable limits are sufficient to measure the expected concentrations of the stated variables.

Detailed protocols for field and laboratory operations at B-sites are being prepared. The B-site field operations are summarized below. B-sites will be manned for 24 hours per day on intensive sampling days. Technicians will verify that all continuous monitoring instruments are operating properly and will change canisters and substrates on a defined schedule. A specially-designed gas and aerosol sampler (the SCAQS Sampler) has been constructed and tested for HNO_3 , NH_3 , SO_2 and the PM-2.5 and PM-10 chemically speciated sampling at B-sites. Media in the SCAQS Sampler will be changed at 0600, 1000, 1400 and 1800 hours local time (PDT in the summer, PST in the fall) and midnight standard time (0100 PDT in the summer, 2400 PST in the fall). The changes beginning at 0600 will help match these samples to the morning rush hour during both summer and fall. The change at midnight will allow these